9th International Conference on Semiconductor Photochemistry

Madrid (Spain) 8-12 September 2025

Book of Abstracts

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SP9

9th International Conference on
Semiconductor Photochemistry

SP9 · Book of abstracts

9th International Conference on Semiconductor Photochemistry

Madrid · Spain · September 8-12 2025

Dear SP9 participants,

Our warmest welcome to Madrid, vibrant capital of Spain, and one of Europe's major cultural and scientific hubs.

On behalf of the Organizing and Scientific Committees, it is our great pleasure to welcome you to the 9th International Conference on Semiconductor Photochemistry (SP9), held on September 8 – 12, 2025.

Launched in 2001 in Glasgow, the international meeting series SP gained over the last 20 years its renown among the most relevant meetings in semiconductor photochemistry and photocatalysis. Hosted in Aberdeen (2007), Glasgow (2010), Prague (2013), Saint Petersburg (2015), Oldenburg (2017), Milan (2019) and Strasbourg (2023), SP takes place in Madrid in 2025.

Following the example of Strasbourg edition, SP9 is preceded, on September 8 2025, by a half-day thematic workshop, aimed mainly at doctoral students and young researchers, focusing on air cleaning and energy applications of photocatalysis and photoelectrochemistry, from theory, materials design and characterization to high-prospect applications. This workshop is organized in connection with CSIC's Hub "Fotocatálisis".

We truly hope that the SP9 program will reflect the high commitment and exceptional profile of the international community working in this field, and selected papers will be published in *Journal of Photochemistry and Photobiology A: Chemistry*, *Chemical Engineering Science* and *Applied Surface Science Advances.*

Finally, lovers of art, history, good food and entertainment be warned: You are very probably going to fall in love! Madrid is definitely well worth a visit, to discover its history, its cuisine and its lively atmosphere. With the Royal Palace, the Prado, Thyssen-Bornemisza and Reina Sofía museums among many others, and the historic heart of the city around Plaza Mayor and Puerta del Sol, Madrid offers a unique blend of heritage and modern urban life.

Outside Madrid, the surrounding region combines cultural richness with natural diversity: from UNESCO World Heritage cities such as Alcalá de Henares and Aranjuez, to traditional gastronomy, wines, and the landscapes of the Sierra de Guadarrama.

For a day, a weekend or for a stay after SP9, be tempted, discover Madrid and its region!

Wishing we all to live an exciting and fruitful conference together,

GRACIAS for attending SP9.

The organizing committee

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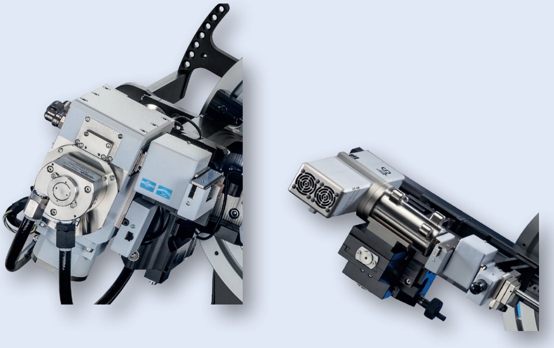

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Thematic Workshop for PhD & Master Students: Photocatalysis for Air & Energy

September 8, 2025, 9:00 - 14:30 h

9:00 – 10:00

Photocatalysis, from water and air treatment to energy: fundamentals and applications
Chantal Guillard, IRCELYON, France

10:00 – 10:45

Photocatalytic elimination of VOCs and other air pollutants: opportunities and limitations
Juan M. Coronado, ICP-CSIC, Spain

10:45 – 11:30

Fundamentals of photocatalytic NOx elimination in air
Silvia Suárez, CIEMAT, Spain

12:00 – 12:45

Photocatalytic hydrogen production
Gerardo Colón, ICMS-CSIC, Spain

12:45 – 13:30

Electrochemical impedance spectroscopy as a powerful tool to understand photo(electro)chemical systems
Miguel García-Tecedor, IMDEA Energy, Spain

13:30 – 14:30

Practical session

Chairs:

Silvia Suárez

Centro de Invetigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT)

Fernando Fresno

Instituto de Catálisis y Petroleoquímica (ICP), Spanish National Research Council (CSIC)

Organized by CSIC Hub "Fotocatálisis"

SP9 program

Monday September 8th

Opening ceremony (17:00 - 17:20)

Plenary lecture 1 (17:20 - 18:10)

Chair: Juan M. Coronado

Metal-Organic Frameworks as Photocatalysts for Solar Fuels Production
Hermenegildo García, Instituto de Tecnología Química, Spain

Session 1 (18:10 - 19:10)

Chairs: Juan M. Coronado & Hermenegildo García

O01: Charge carrier separation and recombination in $WO_3/BiVO_4$ photoanodes
Ivan Grigioni (Università degli Studi di Milano, Italy)

O02: Semiconducting Overoxidized Polypyrrole Nano-Particles for Photocatalytic Water Splitting
VIET DUNG DUONG (Institut de Chimie Physique, France)

O03: Surface-supported All-inorganic Molecular Clusters for Light-driven Water Splitting Reactions
Alexey Cherevan (Technical University of Vienna, Austria)

O04: Amorphous domains and metal centers in graphitic carbon nitride for CO_2 photoreduction
Rudolf Ricka (Technical University of Ostrava, Czech Republic)

Keynote lecture 1 (19:10 - 19:40)

Chairs: Juan M. Coronado & Hermenegildo García

Photo-assisted production of green ammonia-based fuels
Cláudia G. Silva, Universidade do Porto (Portugal)

Welcome reception (19:40)

Tuesday September 9th

Plenary lecture 2 (9:00 - 9:50)

Chair: Patricia García-Muñoz

How light and heat team up to boost heterogeneous catalysis
Nicolas Keller, ICPEES - CNRS / University of Strasbourg, France

Session 2 (9:50 - 10:50)

Chairs: Patricia García-Muñoz & Nicolas Keller

O05: Introducing AIF
David Almazán (Asociación Ibérica de la Fotocatálisis / Eptisa, Spain)

O06: Enhancing NO_x reduction with plasmonic TiO_2+Pt catalysts: The role of TiO_2 support and Schottky barrier height
Gregor Zerjav (National Institute of Chemistry, Slovenia)

O07: Synergistic Photocatalytic-Photothermal Mechanisms in Interfacial Solar Distillation for VOC and SVOC Rejection
Daniela Meroni (Università degli Studi di Milano, Italy)

O08: Anatase and bronze TiO_2 for mineralization of gaseous toluene
Jin Kim Dong (Kyungpook National University, South Korea)

Coffee break (10:50 - 11:10)

Session 3 (11:15 - 13:15)

Chairs: Akihiko Kudo & María José López-Muñoz

O09: $BiVO_4$ and $CuWO_4$-based photoanodes for solar energy conversion
Elena Selli (Università degli Studi di Milano, Italy)

O10: Extension of the (photo)electrochemical working range of WO_3 electrodes to pH 8 by ALD coverage with TiO_2
Tomas Imrich (University of Chemistry and Technology Prague, Czech Republic)

O11: Ionic carbon nitrides in photo(electro)catalysis: achievements and challenges
Radim Beranek (Universität Ulm, Germany)

O12: Microwave-Assisted Synthesis of $ZnO/BiNbO_4$ Heterojunctions for Enhanced Photocatalytic and Photoelectrocatalytic Hydrogen Production
Juliana Souza (Federal University of ABC, Brazil)

O13: Facet-dependent photocatalytic activity of cuprous oxide - the case study of $Cu_2O@TiO_2$ core@shell nanocomposites
Zuzanna Bielan (Faculty of Chemistry, Jagiellonian University, Poland)

O14: 3D-printed ceramic-like photocatalytic membranes with Nb_2O_5 for improved water decontamination
Nuno Gonçalves (University of Aveiro, Portugal)

O15: Synergistic effect of slow photons and localized surface plasmon resonance for enhancement of photocatalytic activity on titania inverse opals
Lei Wang (Faculty of Chemistry, Jagiellonian University, Poland)

O16: Nanospiked ZnO Coatings - Biomimicking Cicada-wing Structures for a Dual Antimicrobial Mechanism
Carlos Sotelo Vázquez (Universidad Rey Juan Carlos, Spain)

Lunch break (13:15 - 14:25)

Keynote lecture 2 (14:30 - 15:00)

Chair: Wojciech Macyk

Material Optimization by Combination of Machine Learning and Analytical Data in the Research and Development of Photocatalytic Materials
Kenji Katayama, Faculty of Science and Engineering (Chuo, Japan)

Session 4 (15:00 - 16:15)

Chairs: Wojciech Macyk & Kenji Katayama

O17: Transient IR measurements as a tool for understanding photoactive materials: what have we learned from studying the photocatalytic Metal Organic Framework (MOF) MIP177?
Yaron Paz (Technion, Israel)

O18: Unravelling the Mechanism of CO_2 Photoreduction by Operando Modulation Excitation IR Spectroscopy
Alberto Ricchebuono (IFP Energies nouvelles, France)

O19: Synthetic Protein Scaffolds for Customizable Chromophore Interactions in Energy Conversion Applications
Luís Duarte (Institute of Chemical Research of Catalonia, Spain)

O20: UV-visible modulation-excitation X-ray absorption spectroscopy to obtain insights in photocatalysts active species: the example of CO_2 reduction by TiO_2 supported Mo oxysulfides
Sébastien Roth (IFP Energies Nouvelles, France)

O21: Unraveling the Role of Cobalt in Photoelectrochemical Oxygen Evolution at Fe_2O_3-CoPi Photoelectrodes via Time-Resolved X-ray Absorption Spectroscopy
Cheshta Chopra (Paul Scherrer Institut, Switzerland)

Coffee break (16:15 - 16:40)

Session 5 (16:45 - 18:00)

Chairs: Josef Krysa & Gian-Andrea Rizzi

O22: Automation of a photoelectrocatalytic wastewater treatment system for the inactivation of antibiotic resistant E. coli
Tony Byrne (Ulster University, United Kingdom)

O23: Reactor design for photocatalytic water-splitting pilot plant using hybrid artificial and natural light
Ahmed Abbas (Texas A&M University at Qatar, Qatar)

O24: 3D-Printed Ti/TiO_2 Electrodes for Enhanced Photoelectrochemical Degradation of Emerging Microcontaminants
Amanda Prado (Rey Juan Carlos University, Spain)

O25: Innovative strategy for in situ and quick photocatalytic measurements on asphalt road surfaces under real-world exposure conditions
Marta Castellote (Institute of Construction Science Eduardo Torroja, CSIC, Spain)

O26: Real-Scale Evaluation of Photocatalytic Pavement Performance for NO_x Abatement in Urban Environments
José Fermoso (CARTIF Technology Center, Spain)

Flash communications 1: F01-F15 (18:00 - 18:45)

Chairs: Andraz Suligoj & Ilaria Berruti

Poster session 1: P001-P015, P041-P095 (18:45 - 20:00)

Wednesday September 10th

Plenary lecture 3 (9:00 - 9:50)

Chair: Jorge Rodríguez-Chueca

Photoelectrocatalytic purification of water: from lab to the real world
Pilar Fernández-Ibáñez, Ulster University, UK

Session 6 (9:50 - 10:50)

Chairs: Jorge Rodríguez-Chueca & Pilar Fernández-Ibáñez

O27: Cavitation-assisted TiO_2 photocatalysis for removal of bisphenols present in water at environmental concentrations
Andraž Šuligoj (University of Ljubljana, Slovenia)

O28: Mechanistic Insights into PFOA Photodegradation: Effects of Catalyst Composition, Surface Modifications, and Irradiation Wavelength
Gabriele Scandura (A-PECS / University of Antwerp, Belgium)

O29: Solar photocatalytic oxidation and heterogeneous ozonation of p-chlorophenol and sunset yellow in a CPC reactor using iron-supported polyurethane foam and pumice beds
Ximena Vargas-Ramírez (Universidad del Atlántico, Colombia)

O30: Photocatalytic Degradation of PFOA: The Role of Adsorption, Repeatability, and Toxicity Outcomes
Lev Matoh (University of Ljubljana, Slovenia)

Coffee break (10:50 - 11:10)

Session 7 (11:15 - 13:15)

Chairs: Chantal Guillard & Tarek Kandiel

Exploring the Dual Photoelectrochemical Activity of Carbon Nitride Films Grown by Electrophoretic Deposition
Damián Monllor-Satoca (Universidad de Alicante, Spain)

O32: Ceria nanostructures as support for metallic clusters: optical properties and catalytic activity
Daniele Ferreira (Universidade de Sao Paulo, Brazil)

O33: Photocatalytic Logic Gate Behavior of Copper-Based Catalysts Driven by NIR and Visible Double-Photon Process
Akashdeep Nath (Laboratoire catalyse et spectrochimie, France)

O34: Hybrid CdSe/ZnS Quantum Dots-Gold Nanoparticles Composites Assembled by Click Chemistry: Towards Affordable and Efficient Redox Photocatalysts
Vincent Maurel (CEA, France)

O35: Combining Quantum Dots with NHCs as Exciton Delocalizing Ligands for boosting their photocatalytic activity
Claire Marchand (CEA, France)

O36: Metal incorporated UiO-66(Zr)-NH_2 frameworks as effective photocatalysts in the hydrogen production
Bartosz Zawadzki (VSB-Technical University of Ostrava, Czech Republic)

O37: MOCHAs: Hybrid Organic-Inorganic Materials for Photocatalytic H_2 Production
Stephen Nagaraju Myakala (Technical University of Vienna, Austria)

O38: CuFe2O4thin films obtained by Supersonic Cluster Beam Deposition on FTO as photocathodes for water splitting and CO_2 reduction
Rizzi Gian-Andrea (Università degli Studi di Padova, Italy)

Lunch break (13:15 - 14:25)

Keynote lecture 3 (14:30 - 15:00)

Chair: Frank Osterloh

Energy transfer in TiO_2 photocatalysis
Francesco Parrino (University of Trento, Italy)

Session 8 (15:00 - 15:45)

Chairs: Frank Osterloh & Francesco Parrino

O39: Facet-Engineered $SrTiO_3$ for Selective Photocatalytic Reduction of Nitroaromatics: Role of Morphology, Metal Co-catalysts, and Doping
Marcin Kobielusz (Faculty of Chemistry, Jagiellonian University, Poland)

O40: TiO_2 Photocatalysis as a Strategy to Control Free-Radical Photopolymerization
Kasidid Yaemsunthorn (Faculty of Chemistry, Jagiellonian University, Poland)

O41: Methane Photocatalytic Conversion to Sustainable Solar Fuels Using Polyoxometalate-Based Catalysts
Andrei Khodakov (Lille University, France)

Flash communications 2: F16-F25 (15:45 - 16:15)

Chairs: Frank Osterloh & Francesco Parrino

Social activity (16:30 - 19:00)

Gala dinner (21:00)

Thursday September 11th

Plenary lecture 4 (9:00 - 9:50)

Chair: Silvia Suárez

Converting Methane to Fuels and Fixing Nitrogen with Atomically-Engineered Plasmon Catalysts
Jennifer Dionne, Stanford University, USA

Session 9 (9:50 - 10:50)

Chairs: Silvia Suárez & Jennifer Dionne

O42: Metal oxides and sulfides photocatalysts for Water Splitting and CO_2 Reduction
Akihiko Kudo (Tokyo University of Sciences, Japan)

O43: Photo-promoted Thermocatalytic Methanol Steam Reforming over Plasmonic Metal Nanoparticles for Hydrogen Production
Tarek Kandiel (King Fahd University of Petroleum and Minerals, Saudi Arabia)

O44: (Photo)thermal chemical looping dry reforming of CO_2 and CH_4 using Cu/Au and
Minoo Tasbihi (TU Berlin / SRH University of Applied Science, Germany)

O45: Photoreforming of organics for H_2 production in the presence of Nb_2O_5 or TiO_2- carbon photocatalysts
Giuseppe Marcì (Università degli studi di Palermo, Italy)

Coffee break (10:50 - 11:10)

Session 10 (11:15 - 13:15)

Chairs: Cláudia Gomes Silva & Jia-Hong Pan

O46: Degradation Pathways Under Hydrothermal Catalysis Assisted by Photocatalysis for energy production
Chantal Guillard (IRCELYON, France)

O47: Photo-reforming of organic compounds for the simultaneous production of hydrogen and value-added chemicals
Ilaria Berruti (CIESOL, Joint Centre of the University of Almería, Spain)

O48: Photoconversion of aqueous carbon dioxide into aliphatic acids using copper and iron oxides at solar-to-chemical conversion efficiency of ~5%
Hyunwoong Park (Kyungpook National University, South Korea)

O49: Dual Photocatalytic Routes for Plastic Waste Upcycling and Mineralization Using Alkalized Carbon Nitride
Sanguk Son (Yonsei University, South Korea)

Controlled Periodic Illumination for Increasing the HER Efficiency Over Metal-TiO_2 Nanoparticles
Francesco Pellegrino (University of Torino, Italy)

O51: A Comprehensive Analytical Model for Front and Back Illuminated Electrodes in Photoelectrochemical Cells
Maria Isabel Díez García (Universidad de Alicante, Spain)

O52: Enhanced Photocatalytic Methanol Formation through Dual Z-scheme Charge Transfer in Titania Nanotubes Co-deposited with Copper and Vanadium Oxide
Samar Al Jitan (University of Antwerp, Belgium)

O53: Hydrogenated TiO_2 nanoparticles: origin of the enhanced photocatalytic properties for the degradation of some pollutants and hydrogen production
José A. Pérez-Omil (Universidad de Cádiz, Spain)

Lunch break (13:15 - 14:25)

Keynote lecture 4 (14:30 - 15:00)

Chair: John Anthony Byrne

Greatly Enhanced Photocatalytic Hydrogen Peroxide Production at High Light Intensity Using Anthraquinone-modified TiO_2
Jonathan Bloh (DECHEMA-Forschungsinstitut, Germany)

Session 11 (15:00 - 16:15)

Chairs: John Anthony Byrne & Jonathan Bloh

O54: Photoelectrosynthetic reactions on n-type semiconductor photoelectrodes
Josef Krysa (University of Chemistry and Technology Prague, Czech Republic)

O55: Light-driven nitrogen fixation to ammonia over aqueous-dispersed Mo-doped TiO2colloidal nanocrystals
Laura Collado (IMDEA Energy, Spain)

O56: Bi-based perovskite for efficient photoreduction of CO_2 to CO
Jie Tian (Guangxi University, China)

O57: Exfoliation of D-A polymers for enhancing their photocatalytic production of H_2O_2
Jorge Plaza Morales (Rey Juan Carlos University, Spain)

O58: Understanding and Enhancing the Photocatalytic NOR on d-Metal-modified TiO_2
Merlin Gutgesell (Technical University Munich, Germany)

Coffee break (16:15 - 16:40)

Session 12 (16:45 - 18:00)

Chairs: Urska Lavrencic Stangar & Yaron Paz

O59: $BiVO_4$ - Liquid Junction Photovoltaic Cell with 0.2% Solar Energy Conversion Efficiency
Frank Osterloh (University of California, Davis, United States)

O60: Transparent ZnO electrodes with near metallic conductivity from solution-based methods: how precursor design is key to scalable technology
Clara Sanchez-Perez (Universidad Rey Juan Carlos, Spain)

O61: Unraveling the Nature of Hole Polarons as OER Intermediates in Titanium Oxides via Ultrafast Optical Spectroscopy
Moritz Lang (University of Colorado [Boulder], United States)

O62: Selenium as a solar material
Peter Vesborg (Danmarks Tekniske Universitet, Denmark)

O63: High-performance perovskite solar cells and the modules
Songyuan Dai (North China Electric Power University, China)

Flash communications 3: F26-F40 (18:00 - 18:45)

Chairs: Moritz Lang & Juliana Souza

Poster session 2: P026-P040, P096-P138 (18:45 - 20:00)

Friday September 12th

Plenary lecture 5 (9:00 - 9:50)

Chair: Freddy Oropeza

Charge separation and stabilisation in photocatalyst materials for solar driven water splitting
James Durrant, Imperial College London, UK

Session 13 (9:50 - 10:50)

Chairs: Freddy Oropeza & James Durrant

O64: When the fate of photogenerated charges matters - classification of heterojunctions in photocatalysis
Wojciech Macyk (Faculty of Chemistry, Jagiellonian University, Poland)

O65: Development of an air purification prototype based on photocatalytic filters with biocidal activity
Gonzalo Sánchez-Domínguez (Instituto de Catálisis y Petroleoquímica, CSIC, Spain)

O66: Local Photoelectrochemistry and Data Modeling for Properties Extraction of Photoelectrodes
Thomas Cottineau (ICPEES - CNRS / University of Strasbourg, France)

O67: Correlation of cyclic voltammetry and impedance spectroscopy models on TiO_2 photoelectrodes
Alejandro Ansón-Casaos (Instituto de Carboquímica, CSIC, Spain)

Coffee break (10:50 - 11:10)

Keynote lecture 5 (11:15 - 11:45)

Chair: Elena Selli

Nanoarchitecture design of photocatalysts towards enhanced photocatalytic activity and stability
Ewa Kowalska, (Faculty of Chemistry, Jagiellonian University, Poland)

Session 14 (11:45 - 13:00)

Chairs: Elena Selli & Ewa Kowalska

O68: Bismuth vanadate coatings produced by magnetron sputtering for water treatment: antimicrobial activity, photocatalytic efficiency, and toxicity assessment
Marina Ratova (Manchester Metropolitan University, United Kingdom)

O69: Distinct Cesium Adsorption Mechanisms of Prussian Blue Analogues with Transition Metals
Soonhyun Kim (Daegu Gyeongbuk Institute of Science and Technology, South Korea)

O70: Highly efficient photocatalyst based on layered LDH/g-C_3N_4 heterojunction for degradation of pharmaceuticals products in water
Angeles Mantilla (Instituto Politécnico Nacional, Mexico)

O71: Photolytic and photocatalytic degradation of lomefloxacin by a Z-scheme photocatalytic system: mechanism and kinetics study
Xuan Li (Khalifa University of Science and Technology, United Arab Emirates)

O72: MOF-semiconductor interaction - How the type of the connection in the heterostructures may control mechanisms of photoinduced processes?
Joanna Kuncewicz (Faculty of Chemistry, Jagiellonian University, Poland)

Closing ceremony

Farewell

Flash & poster communications

No.	TITLE	SPEAKER
F01 P001	Photocatalytic Degradation of Tetracycline in Wastewater Using Ti-$LaFeO_3$ Foam/Powder	Arabbaseri Niloofar
F02 P002	A new approach for developing highly efficient TiO_2 and $SrTiO_3$-based photocatalytic films	Adamowicz Wiktoria
F03 P003	Advanced Oxidation Processes: a powerful tool for nanoplastics removal in water	Jonis Charlotte
F04 P004	$BaTiO_3$–TiO_2 Heterojunction Thin Films via LPD as Photocatalysts for Oxidation	Tekneci Gulsum Efsun
F05 P005	Covalent Organic Frameworks for Solar-Driven Hydrogen Peroxide Production from Water and Air	Bitencourt Gustavo
F06 P006	Dehalogenation reaction over co-catalyst loaded carbon nitride photocatalyst	Hata Kosei
F07 P007	Development of Adsorbent/Photocatalyst Hybrids from Co-Digested Sewage Sludge and OFMSW for CO_2 Capture and pollutants air removal	Lao Zea Angela
F09 P009	Development of Super-Reductant redox photocatalysts	El Ferekh Christian
F10 P010	Differences in photocatalytic activity of modified titanium dioxide during the process of carbon dioxide photoreduction	Sobczuk Konrad
F11 P011	Effect of β-FeOOH modification on the photocatalytic and photoelectrocatalytic performance of BiVO4 in the degradation of pharmaceuticals	Skolotneva Ekaterina
F12 P012	Engineering perovskite-based electrocatalysts through exsolution and galvanic replacement for sustainable alkaline water electrolysis	Velluva Abhijai
F13 P013	Exploring β-5 Lignin Model Compound Photocatalytic Conversion on Carbon Nitride	Liu Junhong
F14 P014	Ferroelectric-Enhanced Photocatalytic Activity of $BaTiO_3$/TiO_2 Semiconductors for Photooxidation and Hydrogen Production Applications	Mreyde Tania
F15 P015	Impact of Pt impregnation on P25 for visible light photocatalytic applications	Martinez Quimbayo Jennyffer S.
F16 P016	Impact of temperature on the efficiency and stability of a TiO_2-based photoelectrochemical cell for solar hydrogen production	Laisné Lucas
F17 P017	Influence of Metal Ratios and Support Materials on the Photo-Fenton Activity of Cu-Fe Bimetallic Catalysts	Kuruvangattu P. Nimisha
F18 P018	Insights into the Coordination Effect on Copper Restructuring in Post-Metalated MOFs During Photocatalysis	El-Roz Mohamad
F19 P019	IR characterisation of powder and membrane-based metal oxide catalysts for photothermal CO_2 reduction	Cavallo Margherita
F20 P020	Mayenite Electride Based Photo-Thermal Catalysts for CO_2-to-Methane Conversion	Hajialilou Ehsan
F21 P021	Metal Ion Effects and Structure Modification Influence on the H_2O2 Production Efficiency of Templated Poly(Heptazine Imides)	Lange Alexander
F22 P022	Optimisation of bi-metallic Pt-Cu/TiO_2 for gas phase CO_2 photoreduction for the production of solar fuels	Khoury Eliane
F23 P023	Optimising WO_3/TiO_2 heterojunctions: A systematic approach for enhanced performance un photocatalytic/photoelectrocatalytic remediation applications	De La Fuente Rodriguez Deyna I.
F24 P024	Oxygen Vacancy Engineering in Nano-CeO_2 for Long-Term Photocatalytic Removal of VOCs	Shin Gahye
F25 P025	Photocatalysis meets exsolution: case study of Cu-based HER co-catalysts	Ladisich Magdalena
F26 P026	Photocatalytic inactivation pathways of E. coli bacteria using bismuth oxyiodide photocatalysts	Martinez-Topete Andrea
F27 P027	K-HEALTHinAIR Project: Annual monitoring of air quality in hospital enviroments and its impact in health.	Rodríguez López Alberto
F28 P028	Photocatalytic ring hydrogenation of furfuryl alcohol over cocatalyst-loaded TiO_2	Inagaki Atsuya
F29 P029	Photocatalytic upcycling of PET into CH_4, H_2 and high-value liquid products	Weisweiller Madeline
F30 P030	Photoelectrocatalysis: A sustainable solution for Resource Recovery from wastewater	Abdolalian Saba
F31 P120	Characterization of lead-free Cs_2SnI_6 perovskite and its ecotoxic effects on isopods	Szalma Lilla

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F32 P032	Photothermal valorisation of CO_2 into methanol over $Cu/ZnO/Al_2O_3$	Jiménez Daniel
F33 P033	Remediation of Indoor Air Quality through Photocatalytic VOCs Removal on construction materials	Alvarez Elean
F34 P034	Shaping Nanocrystals to Understand Catalysis: Case Study of Fe_2O_3 and In_2O_3	Chauhan Jatin
F35 P035	Sol-gel Synthesis of $SrTiO_3$ Enables Enhanced Overall Water Splitting Activity by Al/ Ga doping and in-situ formation of a $SrTiO_3/SrCO_3$ heterojunction	Schumacher Lion
F36 P036	Stability of $CuBi_2O_4$ Photocathodes for Solar-Driven Reduction Reactions	Rusek Jakub
F37 P037	The influence of Ti_3C_2 MXene concentration on the photoactivity of P25	Lakatos Laura
F38 P038	TiO_2 NB/Bi_3O_4Br Z-scheme heterojunction for photocatalytic degradation of paracetamol	Ahmadi Sajad
F39 P039	Water based green sol-gel synthesis of TiO_2 sol for photocatalytic water and air purification coatings with self-cleaning nature	Ayyaz Muhammad
F40 P040	Photocatalytic destruction of Escherichia coli in water using slurry and rotating-disk photocatalytic reactors	Ralphs Kathryn

Poster communications

No.	TITLE	PRESENTER
P041	Effect of silver deposition on the material characteristics and photocatalytic activity of barium titanates	Ágoston Áron
P042	Charge-Carrier Dynamics and Surface Active Sites in Ferrite Thin Films	Al Jitan Samar
P043	The effect of Ag concentration and film roughness on the photocatalytic activity of self-cleaning spin-coated Ag/TiO_2 Films	Alsidran Samah
P044	A Dual-Function $BiVO_4/Sr_2MgSi_2O_7:Eu^{2+},Dy^{3+}$ Heterojunction for Photocatalytic Degradation of Tetracycline and Sustainable Hydrogen Production	Juliana Souza
P045	Solar photoreactor photocatalytic/adsorbents composites	Arfaoui Sarra
P046	Optimizing CO_2 Photocatalytic Reduction: The Role of Carbon Species Equilibrium in TiO_2 Slurries	Ballari M. Milagros
P047	Immobilized Photocatalytic Nanocomposites for Pharmaceutical Wastewater Treatment	Berkesi Daniel
P048	Photocatalytic activity of various BBN-decorated titania composites	Berkesi Daniel
P049	Development and testing of immobilized TiO_2 for water treatment: from the lab to pilot scale	Berruti Ilaria
P050	Bipolar anodization as efficient method for synthesis of gradient titania NTs photoelectrocatalyst	Bielan Zuzanna
P051	Photocatalytic Sand Filters for the Scalable and Continuous Removal of Microplastics from Contaminated Waters	Blazquez-Moraleja Alberto
P052	Catalytic Oxidation of Phenol Using Iron-Supported Illite: Optimization of Parameters for Efficient Wastewater Treatment	Boualam Omar
P053	Charge carriers in $CuW_xMo_{1-x}O_4$ and $CuW_xMo_{1-x}O4/BiVO_4$ heterojunction system via transient absorption spectroscopy	Chellasamy Gayathri
P054	Development of Anti-microbial C_3N_4-ZnO Nanocomposites in Hydrogel coatings for Medical Devices	Chen Ruolan
P055	$CaMn_{1-x}Fe_xO_3$ Perovskites as Catalysts for the Photosensitised Oxygen Evolution	Coronado Juan
P056	Construction of novel MoS_2/BiO_X (X = Cl, Br, I) heterojunctions with an enhanced photocatalytic activity for pollutants degradation	Del Hierro Isabel
P057	Simultaneous degradation of pollutants and H_2 production with photoelectrocatatalysis using 2D/2D TiO2-$BiVO_4$ heterojunctions	Del Hierro Isabel
P058	Printable Photocatalytic Coatings Based on Graphitic Carbon Nitride and Poly(heptazine imide): A Brick-and-Mortar Approach	Dzik Petr
P059	Broad-Spectrum Photocatalytic Removal of Indoor Formaldehyde and Acetaldehyde Using Biochar-TiO_2 (P25) Hybrid Under UV and Dual Visible-Light Irradiation (405 & 450 nm)	Putra Jouvan
P060	Facile Preparation of Nanoporous Polyphenylene Oxide /Photocatalyst Composites and Their Photocatalytic Performance	Fayyaz Zirwa
P061	Photocatalytic upcycling of environmentally relevant PET microplastics for hydrogen generation and value-added chemical synthesis	Fazli Arezou
P062	Application of biochar-supported lanthanide oxide catalysts in heterogeneous photocatalytic treatment of acetaminophen, diclofenac, and metamizole	Hermosilla Daphne
P063	Application of advanced oxidation processes for pharmaceutical residues elimination in wastewater	Garrido Isabel
P064	Remediation of strobilurin pesticide-polluted soils by solar photocatalytic treatment	Garrido Isabel

No.	TITLE	PRESENTER
P065	Simultaneous Removal of Enterococcus faecalis and Tetracycline from Wastewater Using the PMS/N-doped Biochar/Solar Process.	Gaye Cheikh
P066	How interface engineering influences the activity of photoelectrodes in solar energy conversion efficiency	Guler Ali
P067	Anaerobic thermally assisted photocatalytic methanol dehydrogenation in the presence of water vapour: Engineering $SrTiO_3$ photocatalysts.	Haver Yannik
P069	Fabrication and Characterization of WO_3-based gas sensors	Imrich Tomas
P070	Synthesis of MoS_2 and Its Photocatalytic Application in Ciprofloxacin Degradation	Jamil Qasim
P071	Pattern-illumination Time-resolved Phase Microscopy and its Applications for Photocatalytic and Photovoltaic Materials	Katayama Kenji
P072	Photocatalytic Activity and Stability of Carbon Nitride-Pyrite Composites	Kaulbersch Julian
P073	Effects of REEs doping and co-doping on crystal structure, phase and photocatalytic performance of TiO_2	Khaliavka Tetiana
P074	Zr-MOFs based Heterojunction for Enhanced Photocatalytic Methane Oxidation with Nearly 100% Selectivity	Khodakov Andrei
P075	Enhanced Photocatalytic Hydrogen Evolution Under Visible Light Using g-C_3N_4/NiFe Prussian Blue Analog Composites	Kim Minsun
P076	Effect of reaction temperature on production of high concentrations of H_2O_2 over C_3N_4 photocatalyst	Kominami Hiroshi
P077	Evaluation of Muscovite as a Photocatalyst in Aqueous Methanol Solution under UV Light	Kotulková Nela
P078	Preparation and Characterization of Tungsten Oxide Thin Films by Modified Sol-Gel Inkjet Printing for Photoelectrocatalytic Applications	Kralova Marcela
P079	The influence of the substrate on the structural and optical properties of the ordered TiO_2 layers exhibiting a photonic band gap	Kuncewicz Joanna
P080	Microstructural and Chemical Analysis of a Tin Sulphide Homojunction Applied in Thin Film Solar Cells	Carlos Rondón Almeyda
P081	Photocatalytic disinfection efficiency of alkaline earth metal titanates	Lakatos Laura
P082	Efficiency of an advanced oxidation process in the removal of persistent pesticide using an immobilized catalyst	Laoufi Nadia
P083	Solar radiations efficiency for removing xenobiotics in presence of a catalyst suspension	Laoufi Nadia
P084	Advanced Donor–Acceptor Structured Carbon Materials for Sunlight-Driven Hydrogen Peroxide Production via Charge Separation Engineering	Lee Do-Yeon
P085	Water-soluble ionic carbon nitrides for enhanced photocatalysis and other catalytic applications	Liessem Johannes
P086	Graphitic carbon nitride for Hg(II) photocatalytic removal from aqueous solution: influence of precursor and exfoliation	López-Muñoz María José
P087	Preparation of Cu-based TiO_2 and TiO_2/polymeric carbon nitride by hydrogen and nitrogen flow thermal treatment for photocatalytic CO_2 reduction under mild conditions	Majewska Izabela
P088	High-throughput Photocatalytic Reactor with Operando Characterisation for Fast Screening of Materials for the Photodegradation of Water-Borne Pollutants	Maloda Elisante
P089	Black mass from Spent Li-batteries as co-catalyts of C_3N_4 photocatalyst for photoreforming of aqueous solutions of organics	Marcì Giuseppe
P090	Photocatalytic removal of organic pollutants in wastewater using a modified hydrochar catalyst	Marco M. Pilar
P091	Application of Cerium-Based Materials Supported on Different Zeolites for the Photocatalytic Degradation of Methyl Red in Water	Maroto-Valiente Ángel
P092	Fe/Mo bimetallic phases supported on TiO_2 for N_2 reduction into NH_3 by photo-processes	Mary Caroline
P093	On the growth kinetics of Au/TiO_2 Nanowires	Massimo Zimbone Massimo
P094	Development of an air purification prototype based on photocatalytic filters with biocidal activity	Sánchez Domínguez Gonzalo
P096	Comparison of binders in terms of activity and stability of Pt/TiO_2 photocatalyst films for green hydrogen production	Minoo Tasbihi
P097	Evaluation of Ga_2O_3–TiO_2 heterojunction photocatalysts for water treatment	Morales-Castro Katherine
P098	Design of TiO_2 monolithic ceramic photocatalyst for water purification	Negishi Nobuaki
P099	Enhanced adsorption ability and photocatalytic efficiency of supported layered double hydroxides	Ökte A. Neren
P100	Junctions, Charge Transfer Energetics, and Surface Recombination Sites Control Energy Conversion with a Gallium Phosphide Photocatalyst for Hydrogen Evolution	Osterloh Frank
P101	Highly fluorinated g-C_3N_4 for photocatalytic applications	Parmentier Julien
P102	Influence of different antioxidants on the properties of photoactive starch based TiO_2 nanocomposites	Parrino Francesco

No.	TITLE	PRESENTER
P103	Preparation and Characterization of Photocatalytically Active g-C_3N_4 Coatings with Camphor-Induced Porosity for the Efficient Degradation of Antibiotic Pollutants	Patakyova Sylvia
P104	Photooxidation of As(III) in aqueous solution by heteropolyacid-modified natural ilmenite	Pedraza-Avella Julio A.
P105	Photocatalytic conversion of CO_2 in water by alkali-treated natural ilmenite	Pedraza-Avella Julio A.
P106	Electrochemically synthesized copper-tungsten oxides as photo-cathodes for photo-electrochemical water splitting	Penkova Yoanna
P107	Plasma activated water combined with solar disinfection and UVC in the Enterococcus faecalis inactivation	Quintana Terriza Jesús
P109	Immobilisation of photocatalysts on spider silk-based membranes for continuous hydrogen production	Ries Kevin
P110	The chemistry point of view on porous silicon: oxide-free foils with seamless detachability through modulation of electrolyte composition	Sanchez-Perez Clara
P111	Exploring the disinfection of aquaculture matrices by Ga_2O_3/UV-C photocatalysis	Santiago-Espiñeira Pablo
P112	Photocatalytic Oxidation of Anisyl Alcohol using Carbon Nitride/Perovskite Composites	Sampaio Maria J.
P113	Electrodeposited $BiVO_4$ Photoanodes for Solar-Driven Water Splitting and Organic Pollutant Degradation	Sistilii Michelangelo
P114	P-modified g-C_3N_4 for solar-driven photocatalytic H_2O_2 synthesis	Stephen Treesa
P115	Nanostructure ZnO Coatings as Antiviral Surfaces: Influence of Synthesis Methodology on Photocatalytic Efficiency	Sotelo Vázquez Carlos
P116	Thin film design: how does the architecture of rutile and anatase impact the photocatalytic properties?	Spilarewicz Kaja
P117	What determines the photocatalytic activity of g-C_3N_4-Co_xO_y in methanol photoreforming?	Spilarewicz Kaja
P118	Photocatalytic films - from glass to polymers	Šuligoj Andraž
P119	Effect of vanadium pentoxide on the material characteristics and photocatalytic activity of strontium titanates	Szalma Lilla
P120	Characterization of lead-free Cs_2SnI_6 perovskite and its ecotoxic effects on isopods	Szalma Lilla
P121	DACs@TiO_{2-x} for photothermalcatalysis of polyethylene	Tian Jie
P122	Fabrication and Characterization of Dual-Phase Tungsten Oxide Thin Films Made by Direct Patterning	Tomáš Blecha
P123	Photocatalytic Approaches for Plastic Degradation in Water	Valenzuela Laura
P124	A kinetics of singlet oxygen generation on printed photoactive layer	Vesela Maria
P125	UV-B disposable dosimeter	Vesely Michal
P126	Inverse Opal Titania Modified with Gold for Visible-light Photocatalytic Activity	Wang Lei
P127	Photocatalytic pre-treatment of lignin as a strategy to boost biogas production	Wojnarová Petra
P128	Photoactivity of WO_3 films by liquid phase deposition	Wyżga Paweł
P129	On Distinguishing Energy and Electron Transfer in Photocatalytic Processes of Heteroatom-Doped Carbon Dots	Yaemsunthorn Kasidid
P130	Enhanced photodegradation of tetracycline using graphene-like biochar-modified iodine/nitrogen co-doped TiO_2 (g-B/I-TiO_2)	Yuan Ching
P131	$C_3N_3S_3$ (TMT) with cobalt as a new material for photo- and photoelectrochemical water splitting	Zarębska Kamila
P132	Pt-loaded TiO_2 photocatalysts: Correlation between Schottky barrier height and photocatalytic performance	Žerjav Gregor
P133	Photocatalytic Reactor Design for Water Treatment: Organic Pollutant Degradation using 2-methyl-4-chlorophenoxyacetic acid (MCPA) as a Model Compound	Zhou Yan
P134	Characterization of PbS/C/PVDF-based Electrodes for CO_2RR into HCOOH	Kaci Samira
P135	Design of Photocathodes Enhanced Properties for CO_2 photoelectroreduction using Pyramid/Nanowire Texturized Silicon coated with Naostructured PbS Thin Films	Kaci Samira
P136	Cl-doped Polypyrrole for Photocatalytic Green Hydrogen Peroxide Production	Masum Abdullah Al
P137	Enhanced Photocatalytic Hydrogen Evolution via Optimized Coating Strategies for Photo Flow Reactors	Ibrahim Malek
P138	Modeling and Simulation of Decorated Graphene Oxide for Photocatalytic Generation of Hydrogen	El Asame Khaoula
P139	$TiO_2/ZnGa_2O_4:Cr^{3+}/Pt$ composite for high-efficiency photocatalytic hydrogen production	Juliana Souza

Plenary lectures

PL-1

Metal-Organic Frameworks as Photocatalysts for Solar Fuels Production

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Sunlight emitting to the Earth has an estimated power of 172 000 TW and it can provide enough energy to power the planet, whose total power required for human activities is about 20 TW, a similar power that is consumed in Natural photosynthesis. However, besides solar cells to generate electricity and some thermosolar heating applications, other uses of sunlight are still under developed and much scientific advances are needed to implement a suitable solar technology. In particular, sunlight can be used to carry out thermodynamically uphill chemical reactions that can serve to synthesize fuels, broadly denoted by Moore and Gust in the 90s as "solar fuels",[1] following the visionary concept of Ciamician in 1912. The synthesis of green and sustainable solar fuels requires of efficient photocatalysts that by absorbing photons in a wide spectral range convert them into some sort of chemical energy, such as a transient state of charge separation with the generation of electron and holes. After giving a brief overview of the possible role of solar fuels in the new sustainable, green decarbonized energy sources and the current state of the art, I will summarize the structure and properties of several of the photocatalysts studied in our group for solar fuel production from plasmonic metal oxide semiconductors to 2D nanomaterials such as transition metal sulfides and MXenes. Especial attention will be made on the photocatalytic activity of metal-organic frameworks (MOFs)[2] and their heterojunctions with other semiconductors,[2] including MOF-on-MOF, MOF supported on 2D nanomaterials such as graphene-like sheets and MXenes[3] as well as the combination of MOFs and covalent organic polymers (MOF@COFs),[4] highlighting the contributions of our group to the progress of the field.[5] Especial emphasis will be made on the structure-property relationship, the possibilities that MOFs offer to adjust the bandgap energy and the alignment of the frontiers crystal states by controlling the composition and structure of the metal nodes and by adding electron donor or withdrawing substituents on the aromatic linker. The strategy to use the available intracrystalline empty space of MOFs to host co-catalysts will be also commented, showing the contrasting activity of co-catalysts incorporated withing the pores or deposited on the external surface of the MOF crystallites. Most of the presentation will refer to the photocatalytic hydrogen generation and overall water splitting, but advances in the photocatalytic and photothermal carbon dioxide reduction and nitrogen fixation will also be briefly described. The threshold values on efficiency and photocatalyst stability to be achieved for commercial implementation of these photocatalytic processes will also be commented.

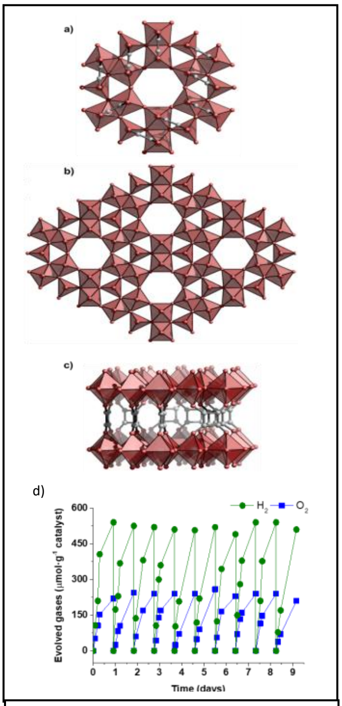

Fig. 1. Structure of IEF-11 and photocatalytic H_2 and O_2 evolution upon irradiation with solar light showing IEF-11 photostability. Reproduced rom Adv. Mater., 2021 adma.202106627

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Acknowledgements

Financial support by the Spanish Agencia Estatal de Investigación, Generalidad Valenciana and European Union (MOF2H, Methasol and ERC Adv. Grant DISCOVERY) is gratefully acknowledged.

PL-2

How light and heat team up to boost heterogeneous catalysis

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The sun is the ideal renewable energy source (albeit intermittent) to be harnessed and integrated into catalytic reactions to make them more sustainable and cost-effective. Primary aims are to accelerate reaction rates to get shorter processing times and higher yields under fixed conditions, to soften the reaction conditions without lowering the yields, to enhance reaction selectivity and catalyst stability. In less than a decade, evidence of cooperative (synergistic) effects between thermal and photonic excitations gave rise to the fastly expanding area of photothermal catalysis with applications for a wide span of reactions [1,2].

As photothermal catalysis rapidly spreads across communities with diverse backgrounds, the term photothermal is often used as a broad umbrella encompassing various phenomena and descriptors (e.g. photothermo-, photo-assisted/driven thermal catalysis), and no unique definition has been established to date [3-5]. The key feature of a photothermal catalyst - regardless of how it is named - is that at least one of its constituents must be light-sensitive.

The dual-mode excitation strategies differ according to the way the thermal energy is supplied to the catalyst, as in any case photons are provided by external excitation. First, both photonic and thermal energies can be provided to the catalyst through a unique source, namely the sun or simulated solar light, low-energy photons (Vis-NIR) increasing the surface temperature, while high-energy photons (UV-Vis) interact with the catalyst for driving reactions. Second, distinct photonic and thermal energy sources rely on the introduction of photons within thermal (conventional) reactors heated following conductive/convective transfer modes. Third, the catalyst itself offers optical heating, where a unique photonic energy supplier provides local heat delivery through a light-to-heat conversion mechanism (self-heating catalyst).

Following an overview of the fundamentals of photothermal catalysis and its underlying mechanisms, the presentation will highlight a series of representative examples across various reactions of interest, drawn from recent literature and studies conducted at ICPEES lab in Strasbourg.

Examples will illustrate mechanisms of heat delivery at both macro- and nanoscale via light-to-heat conversion processes, enabling the activation of thermally driven catalytic reactions. In parallel, electron-mediated mechanisms will be discussed, in which photonic excitation facilitates access to alternative low-energy transition states, thereby modulating reaction kinetics through a newly established dark rate-determining step.

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Photoelectrocatalytic purification of water: from lab to the real world

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Contaminants of Emerging Concerns (CECs) such as pharmaceuticals, personal care products, pesticides, metal-based nanoparticles, and other pollutants, including pathogens, antibiotic-resistant bacteria (ARBs) and genes (ARGs) have been found in treated sewage as well as in drinking water worldwide [1]. A strong effort to develop water treatment systems that remove CECs, ARBs and ARGs in wastewater and drinking water is urgently needed to protect the world environment and public health.

Advanced oxidation Processes (AOPs) have arisen as a promising approach to address the issues related to the presence of Contaminants of Emerging Concern (CECs) and pathogens. Among them, photocatalysis has been regarded as an environmentally friendly alternative to remove pollutants and antibiotic-resistant bacteria. However, only low quantum efficiencies have been obtained (as more than 90% of electrons recombine) so far. Furthermore, most of the photocatalytic studies are focused on using suspended nanoparticles, so to recover these nanoparticles, more units are required, increasing the cost of the photocatalytic process. Electrochemically assisted photocatalysis or photoelectrocatalysis may solve these limitations. PEC processes consist on the immobilisation of a photocatalyst on an electrode that will act as a photoanode. When the energy of the incident radiation is equal to or higher than the band gap energy, an electron is promoted from the Valence Band to the Conduction Band of the semiconductor, giving rise to the generation of electron-hole pairs. An external anode potential, or cell potential, or a constant current density (j) is applied by using a power supply. This allows controlling the Fermi Level of a semiconductor, and therefore band bending, leading to an efficient separation of e—-h+ pairs and reducing their recombination. h+ migrate to the semiconductor surface while photogenerated electrons are transferred to the counter electrode through an external circuit [2].

An efficient design of a PEC system must obey to the following selection criteria: 1) the electrodes must be photo-, chemically-, and mechanical- stable; 2) the systems design has to exhibit a large surface area per unit reactor volume; 3) the fluid dynamic design might allow high flow rates to achieve a homogeneous solution and avoid mass transfer limitations; 4) the reactor design has to minimize ohmic losses and 5) optimal radiation absorption from the point of view of the radiation source-PEC design and the selection of materials.

This paper will present an overview of the design of PEC cells for improved performance for the removal of contaminants of emerging concern and pathogens for water and wastewater treatment applications. The mechanisms governing the degradation of these pollutants will be discussed [3]. Different PEC cell designs [4] and electrode materials will be visited for real-world applications [5-8]. While intensive research has been applied to PEC for water treatment, the scale-up and automation of these systems haven't been examined. For the first time, our group has developed a scaled-up PEC system with an integrated control system to create the first automated PEC treatment (batch) system and make the potential application of PEC to large volumes and real applications feasible. This principle has been demonstrated to be viable for the inactivation of (+5 Log-reduction-value) antimicrobial-resistant bacteria [8].

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Acknowledgements

The authors wish to thank the EU-India H2020 cooperation program and the EU-Marie Curie programme for funding this work under PANIWATER project (RIA GA-820718) and REWATERGY project (MSCA-ITN-EID 812574), and the Royal Society International Collaboration Awards scheme for funding the project ref. ICA-R1-201373.

PL-4

Converting Methane to Fuels and Fixing Nitrogen with Atomically-Engineered Plasmon Catalysts

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With renewable energy becoming more affordable than oil and gas, there is a strong drive to electrify transportation, agriculture, and manufacturing. However, chemical manufacturing has proven difficult to electrify, due to the high energy requirements needed to achieve necessary reactant pressures and temperatures. Plasmonic catalysis is a promising path to enabling industrial chemical production at ambient conditions. Plasmons harness light to generate nanoscale regions of intense electromagnetic fields and hot-carriers that can interact with nearby molecular species and manipulate their chemical transformation via new reaction mechanisms. Here, we present our work investigating plasmonic photocatalysis across length scales, using atomic insights gained via in-situ electron microscopy experiments to inform the reactor-scale production. This talk describes our work on both ammonia synthesis and methane activation. First, we describe AuRu catalysts that enable reactor-scale synthesis of ammonia at ambient conditions under light illumination. Mimicking the process found in natural nitrogenases, these catalysts enable altered intermediate species under light illumination, indicating a plasmonically-modified reaction pathway for NH_x reduction. To understand these catalysts at the atomic-scale, we employ atomic electron tomography to identify chemical active sites and in-situ optically-coupled, gas-cell electron microscopy to probe the catalysts' structural and optical behaviour during active catalysis. We find that the catalysts undergo substantial dynamic atomic rearrangement under gas and light, including increased faceting and formation of core-shell structures. We next describe the use of AuPd bimetallic nanocatalysts for methane-methane coupling with ethene and propylene products. We demonstrate a light-driven mechanistic pathway for minimizing methane combustion and promoting methane oxidation to form desired products. We use 4D scanning transmission electron microscopy combined with tomography to obtain a comprehensive picture of how these AuPd catalysts interface with their TiO_2 support. Across these chemical reactions, we describe how a reactor-to-electron microscope pipeline forms a powerful feedback loop for driving the design of plasmonic catalysts.

Charge separation and stabilisation in photocatalyst materials for solar driven water splitting

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In seminconductor photocatalytic systems for solar energy conversion, a key challenge for efficient operation is the efficient separation and stabilisation of photogenerated charges, and thereby the minimisation of undesired recombination losses. This challenge is particularly great for photocatalytic systems because of the long charge lifetimes required to drive catalysis A further consideration is to minimise the energy losses required to drive this charge separation. My talk will cover examples of recent work from my group addressing aspects of this challenge. I will start by considering the role of polaron localisation / relaxation in driving charge separation in metal oxides, and quantification of the energetic loss associated with this polaron formation. Kinetic competion between polaron formation and ligand field state mediated charge recombination will be highlighted as the key challenge limiting the performance of many visible light absorbing metal oxides. The roles of metal oxide dielectric constant, surface facet energies, traps, ‘photocharging’ and heterojunctions in aiding charge separation in metal oxides will be discussed, drawing on examples from $BiVO_4$ and $SrTiO_3$. I will then go on to discuss charge separation and stabilisation in alternative photocatalyst materials, including organic semiconductor nanoparticles and metal-organic frameworks, highlighting the observation of remarkably long lived charge photogeneration in both systems and their relevance to the efficiency photocatalytic performance.

Keynote lectures

KN-1

Photo-assisted production of green ammonia-based fuels

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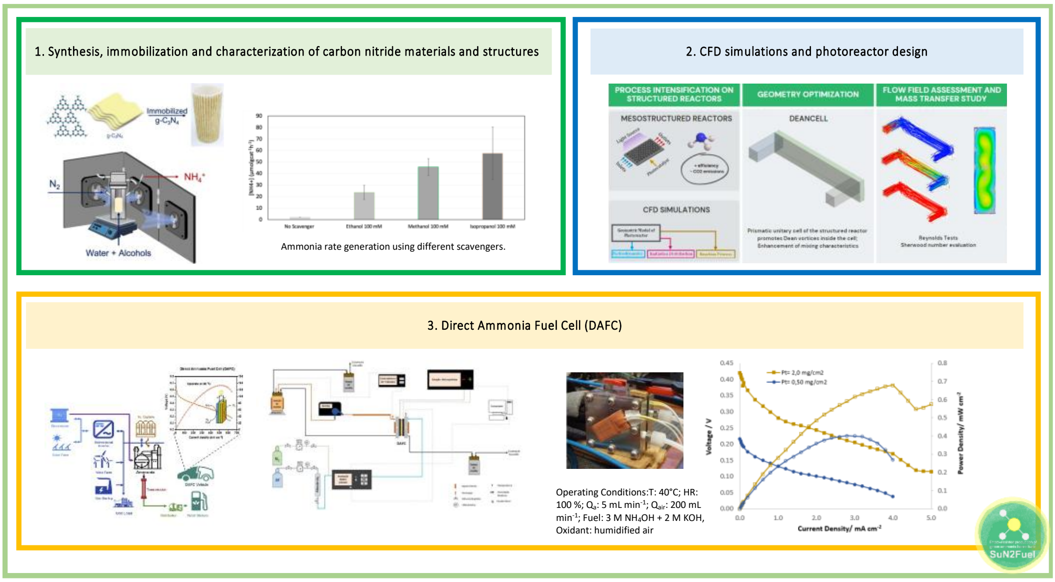
Ammonia (NH_3) is one of the largest-volume synthetic chemicals produced in the world, being mainly employed in the production of fertilizers. It is also a promising indirect hydrogen carrier, much easier to store and transport. Introducing a zero-carbon process to produce ammonia allows for its use as a sustainable energy carrier. Ammonia can also be used directly in fuel cells (DAFCs). The traditional route for NH_3 synthesis follows the Haber-Bosch process, which depends on methane and is energy-intensive, accounting for 1% of greenhouse gas global emissions. Photo-assisted ammonia production is a rising alternative to this industrially set process based on clean technologies and renewable resources, such as sunlight, water, and air. So far, tremendous advancements have been made on the chemistry side of NH_3 photochemical production. For this technology to meet its full potential in building a carbon-free economy, these results must move to the photoreactor side of the equation. For that purpose, the SuN2Fuel project combines fundamental research on catalysts with the design of suitable reactors and respective techno-economic evaluation of the process.

In the project's first stage, a metal-free photocatalyst (exfoliated carbon nitride) immobilized over a 3D-printed structure was tested in a batch photoreactor for ammonia production. For the second task, the unit cell of a mesostructured photoreactor was designed using CFD simulations, and its hydrodynamics and mass transfer behavior was evaluated. Moreover, a DAFC was designed and tested using Pt commercial catalysts. Selected results are illustrated in Figure 1.


1. Synthesis, immobilization and characterization of carbon nitride materials and structures

Ammonia rate generation using different scavengers.

2. CFD simulations and photoreactor design

3. Direct Ammonia Fuel Cell (DAFC)

Operating Conditions:T: 40°C; HR: 100 %; Q_a: 5 mL min^{-1}; Q_{air}: 200 mL min^{-1}; Fuel: 3 M NH_4OH + 2 M KOH, Oxidant: humidified air

Fig. 1. Photocatalytic ammonia production, CFD simulations, and DAFC tests.

The SuN2Fuel project opens up the possibility of using solar-driven technologies for ammonia production using mesostructured photoreactors. Furthermore, the produced ammonia can be directly applied to a DAFC for energy generation.

Acknowledgements
This work is financially supported by national funds through the FCT/MCTES (PIDDAC), under the project 2022.04682.PTDC - SuN2FUEL with DOI 10.54499/2022.04682.PTDC (https://doi.org/10.54499/2022.04682.PTDC). This research was also supported by: UID/50020 of LSRE-LCM - Laboratory of Separation and Reaction Processes – Laboratory of Catalysis and Materials - funded by Fundação para a Ciência e a Tecnologia, I.P. /MCTES through national funds; and ALiCE - LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020). MJS acknowledges FCT funding under the Scientific Employment Stimulus - Institutional Call (DOI:10.54499/CEECINST/00010/2021/CP1770/CT0011).

KN-2

Material Optimization by Combination of Machine Learning and Analytical Data in the Research and Development of Photocatalytic Materials

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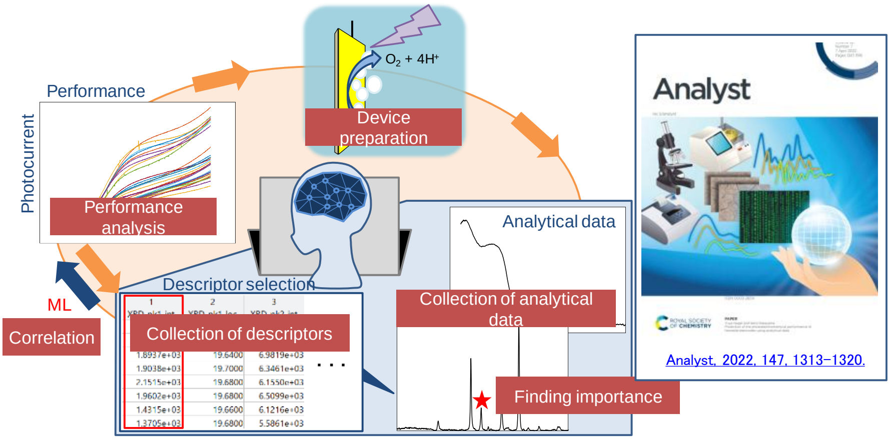
We will introduce the methodology of material optimization using “machine learning (ML) + analytical chemistry data”, which we have been promoting in recent years. Unlike the research on material informatics that is often seen, there are currently almost no studies that can provide scientifically meaningful interpretations using machine learning under conditions where there are only a few dozen data. The reason for good prediction of our methodology is that analytical chemistry data is an extremely good descriptor for materials. Materials science is not so simple that all the answers can be derived from calculations alone, like AI, and it is only by using the analytical methods and data processing that have been cultivated over the years that we can make excellent predictions. In this talk, we will show several demonstrations of how ML can be used to predict and improve the performance of photocatalytic materials.

Photoanodes are promising for solar-driven hydrogen evolution, yet their performance (photocurrent) varies despite identical preparation conditions. This suggests that the unidentified factors could affect the photocurrent of the photoanodes. To clarify the factors, we have developed a scheme to predict the material performance using machine learning (ML) from analytical data, including X-ray diffraction (XRD), Raman spectroscopy, UV/Vis absorption spectroscopy, and photoelectrochemical impedance spectroscopy (PEIS). The analytical data provided features, such as peak intensities or positions, which were used to predict photocurrent values. Then, the ML process identified the dominant factors for performance. This scheme was applied to hematite and bismuth vanadate photoanodes[1,2]. Additionally, we adjusted the operational parameter for the sample preparation based on the dominant factors through ML to enhance the photoanode activity.[3]

In our previous studies, we were unable to determine the contributions of the dominant descriptors to the performance because we used various ML methods. In addition, the use of multiple ML functions could negatively impact the robustness of our scheme when applied to various material data with target values. To address these issues, we have developed a comprehensive and robust approach that encompasses data preprocessing, ML computations, descriptor selection, and importance analysis of the dominant descriptors.[4] The accompanying figure illustrates our recent ML methodology. In this presentation, we explain the calculation scheme and present the results of its application to hematite, bismuth vanadate, and various photoanodes. These results suggest that new results can be produced by successfully fusing the knowledge of materials scientists and analytical scientists, which has been cultivated over many years, with AI.



Hot Article, Analyst, 2024, DOI:10.1039/D4AN00439F.

Fig. 1. Our proposed scheme for optimization of photocatalytic materials.

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KN-3

Energy transfer in TiO_2 photocatalysis

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Photon absorption and charge separation are the primary events in TiO2 photocatalysis. Thereafter, interfacial electron transfer between the excited TiO2 and adsorbed species is generally considered as the driving mechanism for many degradative or synthetic photocatalytic applications. However, in principle both energy or electron transfer can take place upon interaction of an electronically excited species with another in its ground state. In fact, electron and energy transfer are closely related both mechanistically and conceptually, and are qualitatively similar at the initial stage of the interaction. However, they evolve differently along the reaction coordinate depending on several factors. In particular, orbital overlapping is a required condition for electron transfer to occur, while energy transfer can also take place upon long-range dipole-dipole interactions. [1]

Highlighting the existence of energy transfer in TiO2 photocatalysis is a rather challenging task. In fact, often energy and electron transfer mechanisms result in similar product distribution. Moreover, the presence of dispersed particles in photocatalytic systems strongly limit the application of useful characterization spectroscopic techniques, which could highlight the nature of energy transfer driven reactions.

Recently, the occurrence of energy transfer has been inferred in photocatalytic reactions where the nature of some products could not be justified by simply assuming an initial electron transfer step. This is the case of some isomerization reactions [2] or the generation of singlet oxygen in different systems [3, 4]. In those cases, it has been observed that surface silanization of TiO2 promotes energy- over electron transfer. This finding is relevant as it indicates that the modification of the surface of TiO2 could be a simple tool to switch between the two mechanisms and to finely tune the photocatalytic reactivity.

This contribution will provide a survey of paradigmatic examples where energy transfer mechanisms prevail over electron transfer ones. Moreover, the effect of surface silanization on the promotion of energy transfer driven reactions will be discussed on the basis of a recently reported thorough characterization of bare and modified TiO2 samples [5].

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KN-4

Greatly Enhanced Photocatalytic Hydrogen Peroxide Production at High Light Intensity Using Anthraquinone-modified TiO_2

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The reduction of molecular oxygen to hydrogen peroxide is one of the most important reactions in heterogeneous photocatalysis. Not only are peroxides useful chemicals in a variety of applications and oxidation reactions, they are also one of the key active species in environmental remediation.[1] However, the formation of hydrogen peroxide over titanium dioxide (TiO_2) is often observed to be inefficient at higher light intensities.

In thorough kinetic investigations we identified that the surface kinetics are the most limiting factor for the reaction.[2] Bare TiO_2 does not achieve high electron transfer rates, and this leads to inefficiencies at high light intensity.[2] Even polymeric carbon nitride which is reported as an excellent catalyst for oxygen reduction to hydrogen peroxide, is eventually limited at high light intensity.[3]

One of the most efficient known catalysts for hydrogen peroxide formation are anthraquinones (AQ), which are the principal component of the namesake process dominating global peroxide production. In this process, AQ are reduced using hydrogen gas, but electrochemical or photocatalytic reduction is also possible.

Therefore, we explored different AQ compounds adsorbed onto TiO_2 as hybrid photocatalysts for the efficient formation of hydrogen peroxide. Our results reveal that the functional groups on the AQ determine the binding mode and that the binding mode is the key parameter to achieve a high efficiency. All AQ compounds greatly improved the photocatalytic activity, leading to reaction rates up to 3000% higher than bare TiO_2.

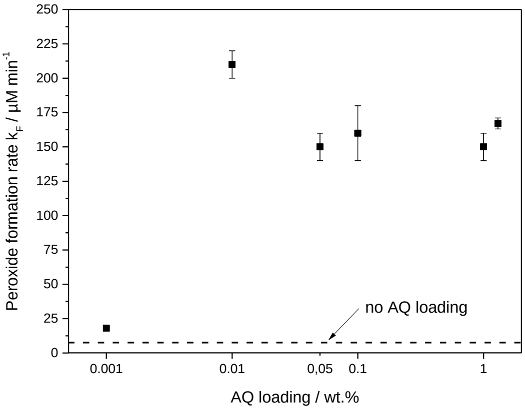

Fig. 1. Photocatalytic reduction rates of molecular oxygen to hydrogen peroxide over TiO_2 catalysts loaded with different amounts of AQ co-catalyst.

Even though it was observed that the AQ compounds were also degraded over time, turnover numbers well over 1000 were achieved, clearly proving a catalytic cycle. With optimization and pH tuning, the degradation could also be greatly suppressed.

Overall, after optimization, extraordinarily high reaction rates of up to 1.9 mM/min were achieved, which is orders of magnitude greater than anything reported for this reaction before. These were achieved with still higher than 20% apparent quantum yield, proving that it is possible to run heterogeneous photocatalytic reactions both fast and efficient at the same time.

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Acknowledgements

The authors are grateful to the German Research Foundation (Deutsche Forschungsgemeinschaft, grant no. BL 1425/1-2) for financial support.

KN-5

Nanoarchitecture design of photocatalysts towards enhanced photocatalytic activity and stability

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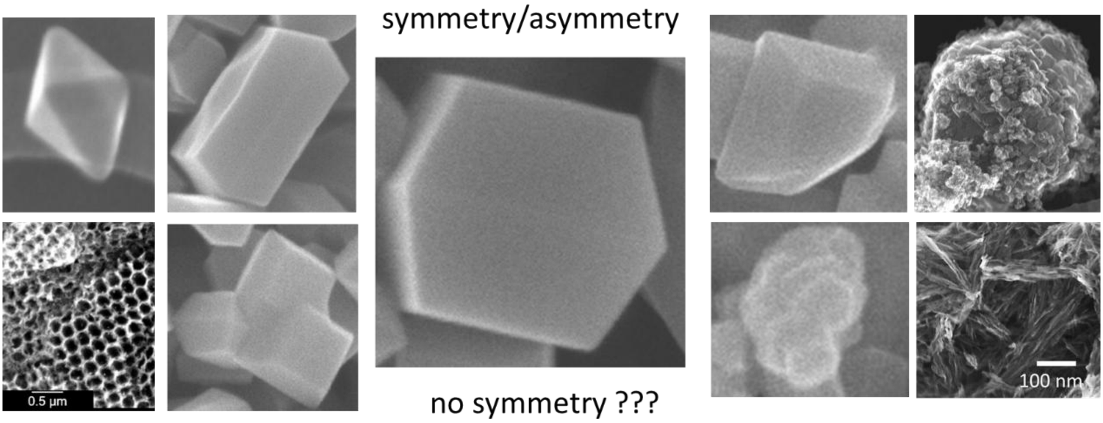
Heterogeneous photocatalysis is considered as a green method for environmental purification and solar energy conversion. However, there are two main problems facing it, i.e., charge carriers' recombination and low efficiency of light harvesting as the most active photocatalysts are usually active only under UV irradiation.

Accordingly, the proper design of photocatalytic materials has been broadly investigated to achieve better photocatalytic performance. Although, it is well known that all surface properties, e.g., specific surface area, crystallinity and crystal/particle sizes, have crucial impact on the overall photocatalytic activity, the resent studies have indicated that the morphology of photocatalysts, including also symmetry and asymmetry aspects, control the photocatalytic performance.

Indeed, our studies on the design of different photocatalysts have confirmed that even a slight change in the photocatalyst morphology might result in significant change in photocatalytic activity [1]. For example, the polydispersity in gold deposits on titania surface is highly recommended for activity under visible-light irradiation (plasmonic photocatalysis) due to enhanced light harvesting efficiency [2]. Moreover, an increase in crystallite size of gold results in an increase in photocatalytic efficiency because of significant enhancement of plasmonic field [3]. Furthermore, the morphology of semiconductor is also highly important, even for photocatalytic activity under vis, where vis response is mainly caused by plasmonic resonance of noble metals rather than semiconductor excitation [4-5]. Additionally, other aspects of morphology (including also symmetry) [6-7] will be discussed during this presentation to underline the importance of photocatalyst properties.



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Acknowledgements

The fruitful collaboration with Marcin Janczarek (Poznan University of Technology), Zhishun Wei (Hubei University of Technology), Agata Markowska-Szczupak (West Pomeranian University of Technology), Maya Endo-Kimura (Hokkaido University), Bunsho Ohtani (Hokkaido University), Kunlei Wang (Nanchang University), Saulius Juodkazis (Swinburne University of Technology), Hynd Remita (Paris Saclay University), Christophe Colbeau-Justin (Paris Saclay University) and Tamer M. Khedr (Central Metallurgical Research and Development Institute) is highly appreciated. This work has received financial support from the Polish National Agency for Academic Exchange within Polish Return Program (BPN/PPO/2021/1/00037) and the National Science Centre (2023/51/B/ST4/01935).

Oral communications

OC-1

Charge carrier separation and recombination in $WO_3/BiVO_4$ photoanodes

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Photoelectrochemical (PEC) water splitting is a way to convert solar light and water into oxygen and hydrogen, a clean energy vector. Bismuth vanadate, $BiVO_4$, is a promising ternary semiconductor oxide employed to assemble photoanodes for the oxygen evolution reaction (OER) in water-splitting devices [1]. When coupled with WO_3, the ability of $BiVO_4$ to absorb visible light up to 520 nm and the excellent electron transport properties of WO_3 allow $WO_3/BiVO_4$ heterojunction photoanodes to outperform the two separate oxide components [2].

In previous studies, we investigated the charge carrier dynamics in the $WO_3/BiVO_4$ system with transient absorption spectroscopy (TAS). By monitoring transient changes in the visible range, we observed the hole dynamics in $BiVO_4$ [3], and by monitoring the mid-infrared, we could track electron dynamics in the two oxides [4]. We also identified wavelength-dependent processes by tuning the wavelength of the excitation pump across the WO_3 absorption edge (ca. 450 nm) [5]. These studies unveiled complex charge transfer processes (**Fig. 1**). Indeed, depending on the excitation wavelength, the band alignment between the two oxides allows charge separation or recombination. Visible light excitation of $BiVO_4$ promotes electrons in its conduction band (CB), which flow into the lower-lying CB of tungsten trioxide, while holes remain separated in the $BiVO_4$ valence band (VB). This process (process 1, **Fig. 1**) decreases charge recombination, extending charge carrier lifetime in the heterojunction, which is beneficial for PEC performance. Conversely, excitation below 450 nm leads to the excitation of both oxides and opens a detrimental recombination pathway that is the recombination between the photopromoted electrons in the CB of WO_3 and the holes in $BiVO_4$ (process 2, **Fig. 1**).

Recently, we reported on the suppression of the detrimental process 2 by exploiting the $BiVO_4$ layer to shield WO_3 from direct photoexcitation [6]. These findings suggest methods to accelerate charge carrier characterizations in semiconductors for PEC applications and to control undesired wavelength-dependent recombination processes.

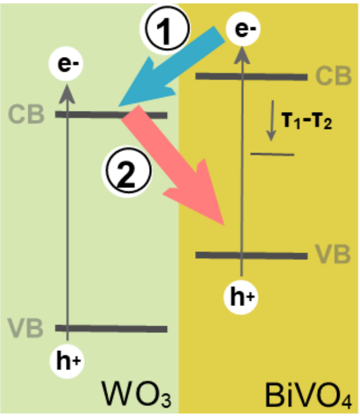

Fig. 1. Charge carrier transfer pathways in the $WO_3/BiVO_4$ heterojunction system: light absorption in $BiVO_4$ promotes electrons (e^-) in the conduction band (CB) and generates holes (h^+) in the valence band (VB). Electrons and holes can recombine (with time constants τ_1 and τ_2) or electrons can flow into WO_3, leading to charge separation (process 1, blue arrow). When WO_3 is photoexcited, electrons in WO_3 CB can recombine with holes in $BiVO_4$ (process 2, red arrow).

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Acknowledgements

This work has received financial support from the Ministero dell'Università e della Ricerca with project 'Charge Transfer Dynamics in Photoactive Materials for Solar Energy Conversion" - CHARM Prot. 20227TKTMY.

OC-2

Semiconducting Overoxidized Polypyrrole Nano-Particles for Photocatalytic Water Splitting

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Harvesting solar energy for photocatalytic water splitting (PWS) into O_2 and H_2 is one of the main research challenges of artificial photosynthesis. Development of organic semiconductors for PWS has become an emerging and auspicious topic in Artificial Photosynthesis, which was largely dependent on inorganic oxides. [1,2,3] However, tedious synthetic pathways are the main problems for optimization of photophysical as well as photocatalytic properties of organic semiconductors. Herein we report radiolytic synthesis of spherical nanoparticles (NPs) of overoxidized polypyrrole (Nano-PPy) and their photocatalytic properties for water splitting. These semiconducting polymer NPs were obtained by oxidation of pyrrole in aqueous solution by HO. radicals induced by γ-radiation. [4]

This material was then characterized as overoxidized polypyrrole since each pyrrole unit contains one oxygen atom, evidenced by X-ray photoelectron spectroscopy (XPS). Scanning transmission electron microscope (STEM) reveals the porous structure inside Nano-PPy when fixed in resin. Diffuse reflectance spectrometry and Tauc's plot analysis provides an optical band gap of *ca.* 1.8 eV while electrochemical studies point out the conduction band at *ca.* -0.5 V and a valence band at *ca.* +1.3 V vs NHE.

Upon visible light illumination higher than 420 nm, Nano-PPy in water catalyzes oxygen evolution reaction (OER), evidenced by the Clark electrode system. Interestingly, during intermittent irradiation and dark phases, we observed a gradual consumption of the evolved O_2 from oxidation of water. This reduce in O_2 was shown to produce H_2O_2. (Fig. 1) These nanoparticles are very stable with cycling.

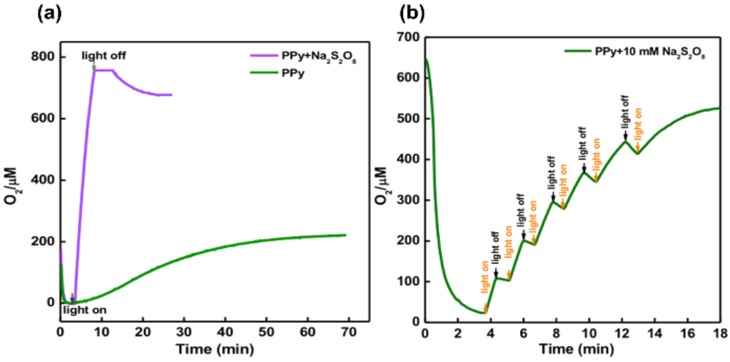

Fig. 1. (a) Time courses of O_2 evolution in the presence of $Na_2S_2O_8$ (10 mM) and in the absence of electron acceptor using Nano-PPy; (b) Alternate cycles of irradiation and dark periods.

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Acknowledgements

This work has been supported by the French National Research Agency ANR (ANR-21- SCOOPE).

OC-3

Surface-supported All-inorganic Molecular Clusters for Light-driven Water Splitting Reactions

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Due to the ongoing global warming and the upcoming energy crises, the exploitation of alternative, renewable energy sources has become a major focus of materials chemistry. The ultimate solution for sustainable energy lies in the concept of solar fuels – commodity chemicals that can be generated from nothing but sunlight and abundant feedstock through heterogeneous photocatalysis. The reactions of water splitting and carbon dioxide photoreduction, however, involve complex multi-electron redox processes that require a rational design of the surface catalytic sites. When working with ill-defined inorganic surfaces, these sites are inevitably hard to study and understand on a truly fundamental level, which limits the development of active and selective photocatalysts.

The field of homogeneous photocatalysis has been evolving independently from its heterogeneous branch, however, it has been much more successful in the purposeful design of organometallic (photo)catalysts assisted by the concepts of coordination chemistry. Molecular photocatalysts, however, face a different set of challenges related to their insufficient redox stability and the need for a molecular photosensitizer required to accomplish the absorption step.

In this talk, I will show that a rational combination of both approaches to photocatalysis can address their challenges and help bridging the gap between the communities. As prime examples of this combination, we employ a diverse set fully inorganic molecular clusters as surface-immobilized co-catalysts for photocatalytic water splitting reactions [1,2]. On one hand, I will discuss covalent attachment of a $[Mo_3S_{13}]^{2-}$ thiometalate anion to photoactive surfaces for light-driven hydrogen evolution [3]. On the other hand, I will present an example of linker-mediated electrostatic binding of $[Co_2W_{11}]^{7-}$ polyoxometalate (POM) onto TiO_2 surface for photocatalytic water oxidation [4]. In-depth characterization will unravel details of cluster immobilization, structural integrity and molecular nature of the attachment. Photocatalytic experiments and mechanistic studies will shed light on their stability and active sites.

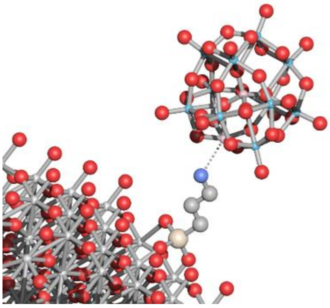

Fig. 1. Schematic of the POM attachment.

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Acknowledgements

This research was funded in whole, or in part, by the Austrian Science Fund (FWF): grant numbers P32801-N and 10.55776/COE5 (Cluster of Excellence MECS)

Amorphous domains and metal centers in graphitic carbon nitride for CO2 photoreduction

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The extensive dependence on fossil fuels, driven by industrialization and rapid population growth, has led to massive CO2 emissions, contributing to the ongoing energy crisis and the amplification of the greenhouse effect [1]. Photocatalytic CO2 reduction is considered a promising approach for converting CO2 molecules into valuable chemicals, such as methane and carbon monoxide. However, practical deployment is hindered by the limited activity and selectivity of current photocatalytic materials [2].

In this work, we successfully synthesized graphitic carbon nitride (g-CN) photocatalysts in various structural states - crystalline, amorphous g-CN, and super-amorphous with integrated metal centers (Co, Ni, Pd, and Mo). These materials were prepared via thermal polymerization, followed by thermal treatment under Ar flow and a final microwave-assisted technique. The prepared photocatalysts were then comprehensively characterized using analytical techniques to evaluate their physico-chemical properties. Finally, their photocatalytic efficiency for CO2 photoreduction was evaluated in a batch-stirred photoreactor. Methane, carbon monoxide, and hydrogen were the main products, quantified using gas chromatograph equipped with a barrier discharge ionization detector (GC/BID).

Our findings reveal that the introduction of amorphous domains enhances charge and increases nitrogen vacancies, both of which significantly boost photocatalytic efficiency. Moreover, the nature of the integrated transition metal sites strongly influences product selectivity and facilitate electron transfer during CO2 photoconversion. These results underline the synergistic effect of structural disorder and metal incorporation in tailoring photocatalytic behaviour, allowing the way toward more efficient and selective CO2 photoreduction systems.

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OC-5

Introducing AIF/PTF

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The *Asociación Ibérica de la Fotocatálisis* (Iberian Photocatalysis Association, AIF) [1], established in 2011, is a non-profit association with an Iberian scope, encompassing the states of Spain and Portugal. Its purpose is to bring together individuals and legal entities involved in the scientific and industrial aspects of photocatalysis and its applications, primarily in construction and urban infrastructure but without disregarding other less comercially developed applications. AIF currently has members such as universities research and technological centres, engineering firms, architects, technology companies, as well as manufacturers and applicators of photocatalytic products.

One of the last milestones of AIF has been to obtain, from the Spanish Ministry of Science, Innovation and Universities, the grant "Plataforma Tecnológica de Fotocatálisis" (Photocatalysis Technology Platform, PTF) [2], started in 2023 with the aim of bringing together all legal entities or individuals involved in the research and application of photocatalytic technologies, such as companies, administrations, engineers, architects, urban planners, healthcare professionals, technological centres, universities, etc., with special emphasis on public-private collaboration.

This prsentation will expand on the activities of PTF are organized within 11 Working Groups that encompass the applications of photocatalysis from low TRLs to market-ready technologies and commercially available products. These include also communication and outreach activities such as the publication of relevant cases of study, the Photocatalysis White Book [3] in both Spanish and Portuguese languages, or the organization of SP9.

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Finantial support from the Spanish State Agency of Research (AEI, 10.13039/501100011033) of the Ministry of Science, Innovation and Universities, through *Plataforma Tecnológica de Fotocatálisis* grant (PTR2024-002885), is gratefully acknowledged.

Enhancing NOx reduction with plasmonic TiO_2+Pt catalysts: The role of TiO_2 support and Schottky barrier height

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The plasmonic properties of noble metals such as gold (Au), silver (Ag) and platinum (Pt) have the fascinating ability to catalyse chemical reactions in wide bandgap semiconductors such as titanium dioxide (TiO_2) when irradiated with visible light [1-4]. When noble metals are illuminated with light equal to or greater than their surface plasmon resonance wavelength (LSPR), they generate "*hot electrons*". These "*hot electrons*" are then injected into the conduction band of the TiO_2 semiconductor. The efficiency of this plasmon-induced injection of "*hot electrons*" depends on the height of the Schottky barrier (SB) at the interface between the noble metal and the TiO_2 carrier [1,2].

Our research pursued three objectives: (i) an in-depth investigation of how the optical, electronic and catalytic properties of TiO_2+Pt catalysts with a 1 wt.% Pt loading are influenced by the textural and morphological features of the TiO_2 support, (ii) the use of X-ray photoelectron spectroscopy (XPS) to accurately determine the height of the Schottky barrier (SBH) and (iii) the investigation of the versatility of the prepared TiO_2+Pt catalysts by using the same material as both a thermal and photothermal catalyst in the reduction of NO_x emissions in the presence of H_2 as a reducing agent, demonstrating an innovative approach to NO_x reduction at low temperatures. Plasmonic TiO_2+Pt solids with 1 wt% Pt and different TiO_2 carriers (anatase nanoparticles (TNP, S_{BET}=86 m^2/g), polycrystalline nanorods (a-TNR, S_{BET}=352 m^2/g) and single-crystalline anatase nanorods (TNR, S_{BET}=105 m^2/g)) were synthesised by the wet impregnation technique. Before testing the catalytic activity of the prepared materials for NO_x reduction, the synthesised solids were subjected to a comprehensive characterisation process using various analytical techniques such as XPS, TEM, SEM-EDX, UV-vis DR, H_2 TPD and others to evaluate the optical, electronic and morphological properties of the materials.

The results of the TEM and H_2 TPD analyses of the investigated solids show that during the wet impregnation process, the nature of the TiO_2 support plays a crucial role in the formation of Pt with different average particle size and particle size distribution, as well as in the formation of Pt oxides with different size, crystallinity and degree of interaction with the TiO_2 support. In particular, the negatively charged surfaces of TNP and a-TNR exhibit a strong affinity for the positively charged $Pt(NH_3)_2^{2+}$ complex, leading to the formation of larger Pt particles, typically 5-7 nm in size. In contrast, the positively charged surface of TNR favours the formation of smaller Pt particles, typically around 2-3 nm in size. The UV-Vis DR spectra of the investigated TiO_2+Pt catalysts show that they can generate charge carriers when exposed to visible light. This phenomenon is attributed to the formation of an SB, which enables the separation and prolonged "lifetime" of charge carriers by transferring "*hot electrons*" generated by visible light from the Pt to the TiO_2 support. The SB heights were found to be 0.38 eV for a-TNR+Pt, 0.41 eV for TNP+Pt and 0.50 eV for TNR+Pt samples. In connection with the thermal catalytic H_2-assisted NO_2 degradation in the temperature range of 30-400°C, different temperature profiles were observed due to the different reduction properties of the catalysts. The TNP+Pt catalyst exhibited the lowest ignition temperature for NO_2 reduction, primarily due to the presence of easily reducible Pt oxides. In contrast, the a-TNR+Pt and TNP+Pt catalysts showed a decrease in NO_2 reduction rate in the temperature range of 120-250°C, which can be attributed to the Pt-catalysed reduction of the TiO_2 support. The TiO_2+Pt catalysts showed improved NO_2 conversion and lower ignition temperatures in the deNO_x process when irradiated with visible light at temperatures below 200 °C, which can be attributed to the Pt-LSPR effect. The highest catalytic activity observed for the TNR+Pt catalyst can be attributed to several factors, including a narrow particle size distribution of the small Pt particles, the absence of Pt-catalysed reduction of the TNR support at higher temperatures and the positive effect of a higher SBH value preventing the re-entry of "*hot electrons*" from the conduction band of the TNR into the Pt particles. The results obtained in the H_2-assisted NO_2 reduction clearly confirm the multifunctional capabilities of the investigated TiO_2+Pt catalysts and demonstrate their versatility for use in hybrid photothermal reaction systems.

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Synergistic Photocatalytic–Photothermal Mechanisms in Interfacial Solar Distillation for VOC and SVOC Rejection

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Solar stills offer a simple, low-cost, and eco-friendly solution for water distillation, making them ideal for desalination of sea- and brackish water in rural areas and emergency contexts. In recent years, interfacial solar distillation (ISD) has gained growing attention due to its ability to enhance desalination efficiency by concentrating photothermal conversion at the water-air interface [1]. This approach achieves higher temperatures and evaporation rates compared to traditional bulk heating methods, while reducing heat loss and improving energy conversion efficiency. Research efforts have mainly focused on optimizing freshwater production through advanced photothermal materials, better thermal insulation, and designs that mitigate salt accumulation [2,3]. However, critical challenges remain, particularly the accumulation of volatile and semi-volatile organic compounds (VOCs and SVOCs) in the collected water [4]. To overcome this issue, the integration of photocatalysis into photothermal evaporators has been proposed [5]. Photocatalysts can enable the light-driven degradation of organic contaminants, potentially improving water quality. However, the underlying mechanisms are still unclear, and the lack of standardized testing conditions affects the comparability of literature studies. This study investigates the mechanisms at play in hybrid photothermal-photocatalytic evaporators. Immobilized TiO_2 was selected as a photocatalyst due to its well-characterized and widely studied photocatalytic pathways. A range of target pollutants—including dyes and phenolic compounds—were selected based on their volatility, environmental relevance, and degradability. Our results show that commonly used dyes such as methyl orange and Rhodamine B, although prevalent in the literature, are completely rejected by photothermal evaporation alone due to their low volatility, thus limiting their usefulness in evaluating photocatalytic contributions in such context. In contrast, phenolic compounds proved to be more suitable targets, as they tend to accumulate in the condensed water and are partially removed through photocatalysis. To disentangle the contributions of photothermal and photocatalytic pathways to the distillate concentration of phenols, we compared systems with interfacial, submerged, and vapor-exposed photocatalyst configurations. As expected, photocatalysis reduced the concentration of the parent compound in the distilled phase by lowering its concentration in the liquid feed. However, we also observed a reduction in the total concentration of aromatic species in the distillate. To clarify this phenomenon, reaction intermediates were identified and tracked in both the liquid and vapor phases. Our findings reveal that photocatalytic oxidation produces less volatile intermediates, which are more effectively rejected during evaporation. Thus, photocatalysis and photothermal effects act synergistically to achieve effective purification of water, not only from phenolic compounds but also from their degradation byproducts. Depending on the placement of the photocatalyst within the photothermal evaporator, photocatalytic degradation of VOC-rich vapors can also occur. We specifically investigated the photocatalytic treatment of vapors above the evaporator in solar stills, particularly in water matrices containing pollutant mixtures. These findings were applied to the development of a photothermal evaporator incorporating a cost-effective salt-rejection and thermal insulating support, and an immobilized photocatalyst for the optimal rejection of inorganic compounds, SVOCs, and VOCs.

Overall, this work provides mechanistic insight and practical guidance for the development of next-generation solar evaporators with integrated photocatalytic functionality, supporting their application in sustainable water treatment and climate change adaptation.

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Acknowledgements: We acknowledge financial support under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.1, Call for tender No. 1409 published on 14.9.2022 by the Italian Ministry of University and Research (MUR), funded by the European Union – NextGenerationEU– Project Title COPE - COmposite nanomaterials coupling Photothermal Evaporation and photocatalysis for durable water purification systems – CUP G53D23006660001 - Grant Assignment Decree No. 1384 adopted on 01.09.2023 by the Italian Ministry of Ministry of University and Research (MUR).

OC-8

Anatase and bronze TiO_2 for mineralization of gaseous Toluene

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Heterojunction formation between anatase (A) and rutile (R) TiO_2 is widely recognized as a benchmark strategy for improving photocatalytic performance. In this study, we synthesized anatase-bronze (AB) TiO_2 heterojunctions via hydrothermal and annealing processes using cost-effective commercial anatase TiO_2. The resulting AB-TiO_2 exhibited exceptional photocatalytic activity for toluene mineralization and demonstrated strong resistance to deactivation. Comparative analysis of 10 different TiO_2 samples—including bare and Pt-deposited A-, R-, B-, and AR-TiO_2 confirmed that AB-TiO_2 outperformed all counterparts in both activity and durability. Structural characterization revealed the presence of highly active {001} facets, which facilitate hydroxyl radical generation and promote oxygen vacancy formation for enhanced O_2 adsorption. Transient absorption and time-resolved photoluminescence spectroscopies elucidated the charge carrier dynamics, while density functional theory (DFT) calculations identified anatase as the dominant catalytic surface in AB-TiO_2. The superior photocatalytic performance of AB-TiO_2 is attributed to its optimized charge separation and synergistic photochemical and catalytic properties.

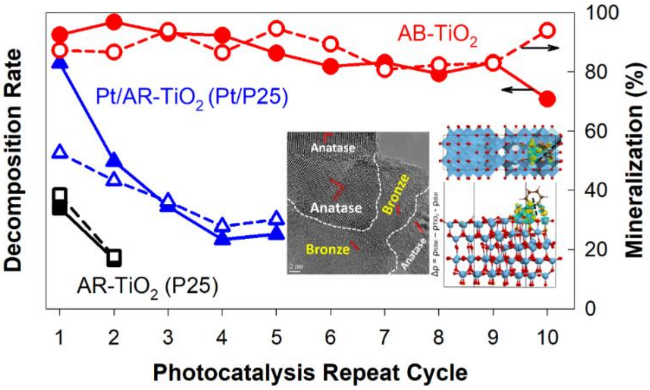

Fig. 1. Photocatalytic activity of AR-TiO_2 (P25), platinized AR-TiO_2 (Pt/P25), and AB-TiO_2over 10 consecutive cycles (Inset: Material characteristics of AB-TiO_2).

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OC-9

$BiVO_4$ and $CuWO_4$-based photoanodes for solar energy conversion

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Solar energy conversion into hydrogen is a valuable approach to capture the energy that is freely available from sunlight and to turn it into a clean fuel. To this aim, photoelectrochemical (PEC) water splitting is an established powerful technology requiring the development and optimization of efficient oxide-based semiconductor photoanodes for water oxidation, the kinetic bottleneck of the overall PEC water splitting process.

Two ternary metal oxides able to absorb a relatively large portion of the solar spectrum, i.e., $BiVO_4$ and $CuWO_4$, have been thoroughly investigated as photoanode materials by our research group, employing up-to-date time-resolved optical spectroscopic and electrochemical techniques to shed light on the photogenerated charge carrier dynamics driving PEC processes, in relation to the PEC performance under different conditions.

Bismuth vanadate has emerged as a leading photocatalyst for the oxygen evolution reaction despite its poor electron transfer ability and slow water oxidation kinetics. We found that the PEC performance of $BiVO_4$ can be largely improved either

i) by coupling it with WO_3 in a heterojunction, for which transient absorption spectroscopy (TAS) revealed an excitation wavelength-dependent efficiency in photoproduced charge separation [1,2] and different hole lifetimes under different operando conditions [3] or frontside/backside irradiation [4-6]; or

ii) by doping it with hexavalent metal ions such as Mo^{6+}. In this case, the largely improved water oxidation activity results from multiple factors, including increased electron conductivity of $BiVO_4$, longer lifetimes of photoproduced holes and surface effects reducing the interfacial charge transfer resistance [7,8].

On the other hand, an efficient use of $CuWO_4$ as photoanode material requires to overcome its severe internal charge recombination, which is due to the existence of intra gap states, acting as electron traps. This was ascertained by us through a PEC investigation coupled with ultrafast TAS analysis [9], which was performed also with differently thick $CuWO_4$ layers in the presence of sacrificial agents or cocatalysts [10].

A partial Mo^{6+} for W^{6+} substitution results in $CuW_{1-x}Mo_xO_4$ electrodes (x = 0 - 0.8) with enhanced visible light-induced photoactivity compared to pure $CuWO_4$, a 1:1 W:Mo molar ratio leading to an optimal PEC performance and photoactivity up to 650 nm [11]. A recent intensity modulated photocurrent spectroscopy analysis unequivocally demonstrates, in full agreement with the results of PEC measurements in the presence of a hole scavenger, that the poor charge carrier separation efficiency within the material bulk, limiting the PEC performance of $CuWO_4$, undergoes a 4-fold increase upon 50 at.% molybdenum for tungsten substitution, without producing any significant change in the optimal injection efficiency of these materials [12].

Best performing $CuW_{0.5}Mo_{0.5}O_4$ combined with $BiVO_4$ in a heterojunction exhibits a definitely superior PEC performance compared to the individual components, with a synergistic charge separation improvement in the 350-480 nm range under frontside irradiation through a $BiVO_4$ layer thick enough to absorb most of the incident light [12].

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Acknowledgements

This work received financial support from MUR (Italy), through the PRIN CHARM (No. 20227TKTMY) project.

OC-10

Extension of the (photo)electrochemical working range of WO_3 electrodes to pH 8 by ALD coverage with TiO_2

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In our previous work [1], we developed WO_3 photoanodes with stable photocurrent-time behaviour in acidic media (perchloric acid). Such WO_3 photoanodes could have an application in the photoelectrochemical degradation of organic pollutants dissolved in water if they are stable in the neutral range (pH 6–8). However, WO_3 dissolves at pH around 6 and above [2, 3]. A possible solution could be the application of a protective overlayer consisting of a chemically more resistant semiconductor (TiO_2 or SnO_2) with a wider bandgap acting as window material in the front side illumination mode.

The present work aimed to check whether the above considerations are valid by experimentation with ALD coverage of WO_3 photoanodes with protective TiO_2 films of various thicknesses. Besides monitoring the photocurrents of as-obtained and covered photoanodes, it was the purpose of capping with TiO_2 to see whether in phosphate buffer (pH 8) stabilization against dissolution and photocorrosion can be achieved.

Table 1. Dissolution rates and Faradaic efficiencies of WO_3 photocorrosion in 0.1 M phosphate buffer (pH 8). The initial WO_3 layer thickness was 4300 nm.

Coverage by TiO_2 ALD	Conditions	Dissolution rate /$nm \cdot h^{-1}$	Thickness decrease/nm	Charge /C	Faradaic efficiency
none	4 h dark	252	1008	-	-
none	4 h 0.9 V* light	-	2112	3.04	0.82
none	1 h 0.9 V* light	-	1314	2.25	1
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20 nm	4 h dark	0.58	2.3	-	-
20 nm	1 h 0.9 V* light	-	28	0.95	0.064
50 nm	1 h 0.9 V* light	-	9	0.12	0.17
20 nm annealed$^\$$	1 h 0.9 V* light	-	61	1.8	0.076
50 nm annealed$^\$$	1 h 0.9 V* light	-	16	1.1	0.033

*potential *vs*. Ag/AgCl, electrode area 1 cm^2; $^\$$annealed at 500 °C for 1 h in air

The coverage of WO_3 by protecting TiO_2 layers using ALD was shown to be a means of extending the operational pH range in (photo)electrochemical operation up to pH 8. In contrast to α-$Fe_2O_3|TiO_2$ photoanodes where photocurrents are strongly decreased with increasing thickness of ALD TiO_2 overlayers [4–6], in the case of $WO_3|TiO_2$ such capping layers led to much less decrease of photocurrents. This is ascribed to a more favourable relative position of valence band energies of the two semiconductors in the latter case, allowing easier passage of photogenerated holes from the absorber material to the capping layer. The dissolution efficiency of photocorrosion in pH 8 solutions decreased by a factor of 20 when the WO_3 electrodes were covered with TiO_2. Consequently, the presence of 20 nm thick capping layers extended the “lifetime” of photocurrents in pH 8 solutions from 3 to 25 hours. This is a proof of concept as to the use of capping layers for the suppression of (photo)corrosion.

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Acknowledgements

This work was supported by the project "Sensors and Detectors for Future Information Society – SENDISO reg. n. CZ.02.01.01/00/22_008/0004596" by the Programme Johannes Amos Comenius, call "Excellent Research". This work was also supported by the Czech Science Foundation (project number 23-05266S).

OC-11

Ionic carbon nitrides in photo(electro)catalysis: achievements and challenges

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Ionic carbon nitrides based on poly(heptazine imides) (PHI) represent a vigorously studied class of polymeric materials with possible applications in photocatalysis and energy storage. However, most of the studies reported so far have been carried out using particulate PHI suspensions, since the fabrication of photoelectrodes was challenging due to poor adhesion, unsatisfactory mechanical stability, inhomogeneity and low conductivity of the resulting coatings.

Recently, we demonstrated, for the first time, the fabrication of binder-free, mechanically robust and photoelectrochemically stable PHI photoanodes via an aqueous sol–gel technique using water-soluble PHI [1] as precursor. The excellent photoelectrocatalytic performance of the resulting photoanodes is demonstrated in alcohol reforming and highly selective (~100 %) photooxidations with exceptionally low photocurrent onset potentials (< 0 V vs. RHE) [2]. Using in operando transient photocurrents and spectroelectrochemical photoinduced absorption measurements, we discovered that light-induced accumulation of long-lived trapped electrons within the PHI film leads to effective photodoping of the PHI film, resulting in a significant improvement of photocurrent response due to more efficient electron transport [3]. While photodoping has been previously reported for various semiconductors, it has never been shown before for carbon nitride materials. Furthermore, we found that the extraction kinetics of untrapped electrons are remarkably fast in these PHI photoanodes, with electron extraction times (ms) comparable to those measured for commonly employed metal oxide semiconductors.

The contribution will discuss the intriguing properties of ionic carbon nitride materials, in particular with respect to our recent theoretical insights into their peculiar photophysics [4-6].

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OC-12

Microwave-Assisted Synthesis of ZnO/$BiNbO_4$ Heterojunctions for Enhanced Photocatalytic and Photoelectrocatalytic Hydrogen Production

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Bismuth niobate represents a functional class of materials that exhibits chemical and electrochemical stability, as well as photoelectronic activity. These properties can be explored in various applications, including photocatalysis. Its efficiency can be improved by coupling it with other metals or metal oxides.

This work explores the fabrication of ZnO/$BiNbO_4$ heterojunctions using a microwave-assisted technique, which significantly reduces processing time and energy consumption. ZnO nanorod films were synthesized in 48 minutes and combined with $BiNbO_4$, which was obtained in 30 minutes, forming two heterojunctions: $BiNbO_4$/ZnO (without annealing) and $BiNbO_4$/ZnOT (annealed).

The detailed characterization of the synthesized materials, including X-ray diffraction, scanning and transmission electron microscopy, confirmed the formation of a heterojunction between the components. Kelvin probe force microscopy, X-ray photoelectron spectroscopy, Ultraviolet photoelectron spectroscopy, optical analysis, and Mott-Schottky plots indicate the formation of an S-scheme structure, which increases the separation of photogenerated charges. This hypothesis was also supported by time-resolved microwave conductivity measurement, time-resolved fluorescence, and photoluminescence studies. However, slight differences in the properties indicated that the thermal treatment increased the coalescence and stability of the BiNbO4/ZnOT. As a result, $BiNbO_4$/ZnOT has higher photo(electro)catalytic activity. The oxygen evolution reaction under photoelectrochemical conditions and hydrogen evolution study under photocatalytic conditions further support that the BiNbO4/ZnOT heterojunction has the highest performance. As a result, the heterojunction demonstrated photocatalytic activity for hydrogen production that is 3.5 times higher than that of bare ZnO and 2 times higher than that of $BiNbO_4$.

These results highlight the potential of $BiNbO_4$-based materials for hydrogen production, with relevance for Brazil, given its significant niobium reserves and the strategic importance of developing new applications for this metal.

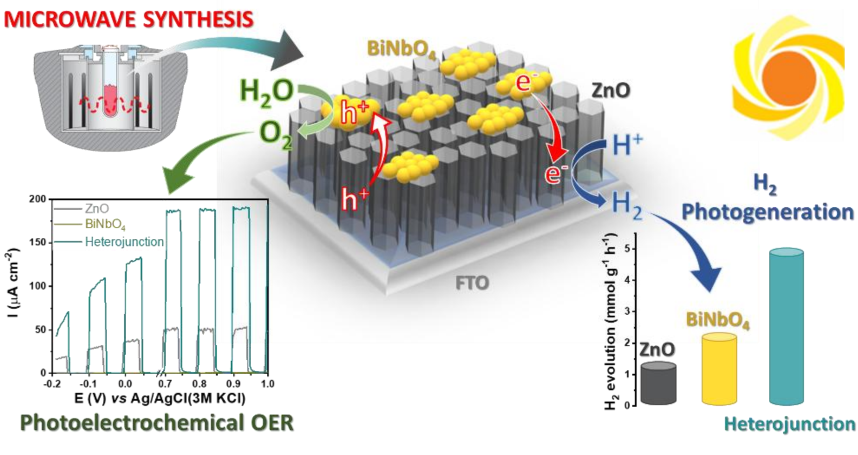

Fig. 1. Schematic representation of the heterojunction $BiNbO_4$/ZnOT and its photo(electro)chemical activity towards hydrogen production

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This work has received financial support from the FAPESP grant 2024/18336-0.

Facet-dependent photocatalytic activity of cuprous oxide - the case study of $Cu_2O@TiO_2$ core@shell nanocomposites

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Recently, more and more efforts have been put in nanoarchitecture design of photocatalysts, especially those with exposed facets. Cuprous oxide (Cu_2O) is a notable example, exhibiting different facets such as {111}, {110}, and {100}, each affecting its photocatalytic performance. However, Cu_2O suffers from photooxidation under prolonged light exposure, limiting its standalone use. Therefore, there is an urgent need for effective and simple method for Cu_2O protection, while at the same time its photocatalytic properties should still be used under visible-light irradiation. Nowadays, a lot of effort is put into exploring heterostructures combining Cu_2O with more stable photocatalysts like TiO_2 to enhance its stability and activity [1-2]. Nevertheless, forming a simple composite still does not guarantee the photostability of cuprous oxide.

Therefore, core@shell heterostructures with faceted cuprous oxide as a core and titanium(IV) oxide as a shell were investigated. The dependence between exposed facets of Cu_2O nanoparticles and the physicochemical and photocatalytic properties of the materials (unmodified Cu_2O as well as obtained $Cu_2O@TiO_2$ core@shell structures) were studied. Moreover, the stability of the composite, and clarification of the photocatalytic mechanism during different reactions (both reduction and oxidation ones), were discussed in details.

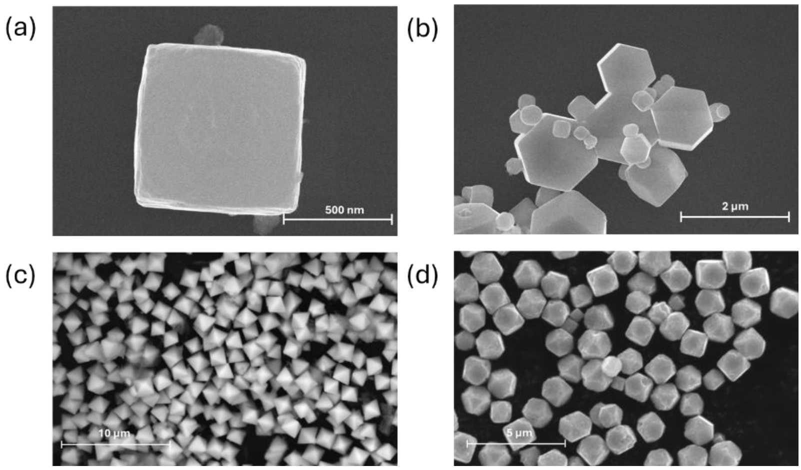

Fig. 1. SEM images of obtained faceted Cu_2O structures: (a) cubes, (b) rhombic dodecahedrals, (c) octahedrals, and (d) truncated cubes.

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3D-printed ceramic-like photocatalytic membranes with Nb_2O_5 for improved water decontamination

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Semiconductor photocatalysts represent a powerful technology for degrading persistent water pollutants. Among these, niobium pentoxide (Nb_2O_5), a non-toxic, eco-friendly metal oxide with strong oxidizing capabilities, has garnered significant research interest. Nb_2O_5 is an n-type semiconductor whose efficacy in removing water contaminants is enhanced by its unique Lewis and Brønsted acid sites. Furthermore, the specific crystalline phase and properties of Nb_2O_5 are strongly influenced by its preparation conditions [1].

Despite the demonstrated potential of semiconductor photocatalysts, practical water treatment applications are hindered by challenges in catalyst recovery after use. Immobilizing the photocatalyst onto a substrate overcomes this limitation, potentially enhancing stability, efficiency, and reusability, thereby improving cost-effectiveness.

In this context, inorganic polymers (IPs) emerge as attractive support materials [2]. These ceramic-like materials are low-cost, environmentally friendly, and possess high mechanical and chemical stability. They are typically synthesized at near-ambient temperatures through the alkaline activation of aluminosilicate precursors, such as metakaolin. By employing additive manufacturing techniques, it is possible to fabricate IP membranes with precisely engineered architectures, controlling pore size, distribution, and interconnectivity [3,44].

This study focuses on development of 3D-printed photoactive IPs membranes incorporating Nb_2O_5 via direct ink writing (DIW). Their performance was evaluated for removing selected emerging contaminants (ECs) in a continuous flow system under LED light. Initially, amorphous Nb_2O_5 was synthesized using a hydrothermal method. Subsequent thermal treatments yielded different crystalline phases: pseudohexagonal (PH-Nb_2O_5), orthorhombic (T-Nb_2O_5), and monoclinic (H-Nb_2O_5), based on the post-synthesis thermal treatment. The impact of these phases on the photocatalytic activity was investigated for the degradation of ciprofloxacin drug, selected as a model pollutant. A properties-activity correlation study was stablished and the operational parameters optimized.

The optimal phase, T-Nb_2O_5, was then incorporated into the 3D-printed ceramic-like structures using two distinct approaches: i) direct mixing into the printable ink and ii) immobilization onto the surface of pre-printed structures. The effect of catalyst loading amount and preparation method on the functional membrane activity towards ciprofloxacin was investigated. The photoactive membranes were fully characterized and tested for the removal of simultaneous emerging water pollutants in a continuous flow reactor under UV LED irradiation. These results highlight additive manufacturing as a promising route for designing customized porous ceramic-like membrane supports for semiconductor photocatalysts, leading to enhanced photocatalytic performance in water pollutant degradation.

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This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). NG acknowledge the funding from the European Union’s Horizon Europe research and innovation programme under the Marie Skłodowska-Curie Actions PF grant agreement No 101065059 and FCT 2022.06593.CEECIND/CP1720/CT0024 (DOI 10.54499/2022.06593.CEECIND/CP1720/ CT0024).

OC-15

Synergistic effect of slow photons and localized surface plasmon resonance for enhancement of photocatalytic activity on titania inverse opals

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Photonic crystals, particularly inverse opals, have been considered as a potential structure for efficient light manipulation. Enhancement of light harvesting through a unique optical property, named slow photon effect, appearing at the edge of photonic bandgap (PBG), has been recently applied in the field of photocatalysis [1]. Our previous study demonstrated a notable increase in photocatalytic efficiency when the PBG edge matched with the photoabsorption of TiO_2 [2]. However, TiO_2 is mostly valued for its UV photoactivity, thus the development of its visible-light response has been an inevitable topic. Therefore, plasmonic nanoparticles with their localized surface plasmon resonance (LSPR) effect are a great prospect for visible light activity of inverse opal titania (IOT) [3].

In this regard, combination of slow photon effect as a property of IOT with LSPR coming from Au nanoparticles (Au NPs) was studied in order to develop a well-organized photocatalytically active structures able to utilizing visible light.

W**ell-established Au-decorated inverse opal titania (Au/IOT) films on a** glass substrate were obtained by co-assembly method. **Unlike a conventional synthesis process,** with three consecutive steps, i.e., **(i) formation of opal template; (ii) infiltration of titania; and (iii) removal of opal template,** this method **combines opal formation and infiltration** steps. Moreover, Au NPs deposition was implemented simultaneously during the structure formation, allowing the **cracks** elimination.

The synthesized IOT and Au/IOT exhibit well-ordered face-centered-cubic structure, as shown in **Fig.1**. Although the thickness of the films is rather low, obtained materials still exhibit great photoactivity under UV/vis irradiation in various reaction systems, including oxidative acetic acid degradation and terephthalic acid hydroxylation. Furthermore, Au NPs position dependence (on the surface or embedded in the wall structure) on Au/IOT photocatalytic activity was also investigated. What is also worth to mention, both optical properties and photocatalytic activity were tested in a specially designed angle-dependent system in order to examine photonic properties of obtained materials.

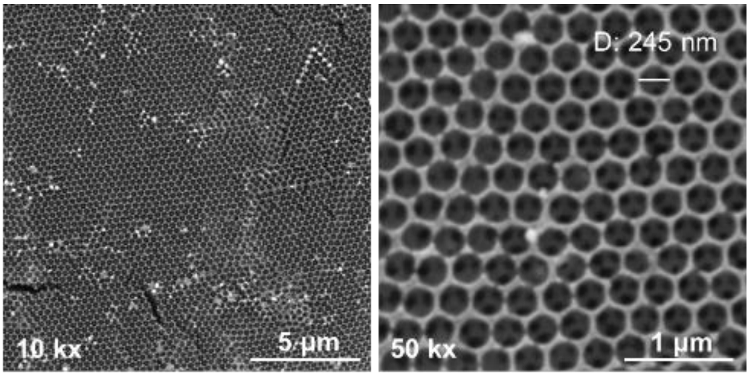

Fig. 1. SEM images of Au/IOT film under two different magnifications.

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OC-16

Nanospiked ZnO Coatings - Biomimicking Cicada-wing Structures for a Dual Antimicrobial Mechanism

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Zinc oxide (ZnO) nanostructures are at the forefront of cutting-edge applications in optoelectronic, photocatalytic, and antibacterial applications. We present the first successful synthesis of well-aligned ZnO nanorods (NRs) with spiky terminations via aerosol-assisted chemical vapour deposition (AACVD), mimicking the morphology of the wings of Cicadas. This novel approach achieves precise control over nanostructure alignment and morphology, addressing key limitations in ZnO-based functional coatings to deliver nanostructured coatings with a dual antimicrobial mechanism.[1]

Our innovative two-step AACVD process enables precise control over nanostructured alignment and morphology. By engineering a c-axis-oriented ZnO seed layer, we drive the growth of high-aspect-ratio NRs with sharp, concave apexes purely along the [0001] direction, significantly enhancing surface reactivity.[2] Structural analysis via SEM, HRTEM, and XRD confirms uniform alignment and phase purity (**Fig. 1**), while optical characterisation reveals a blue-shifted bandgap (~3.65 eV), indicative of quantum confinement effect at the nanospike tips.

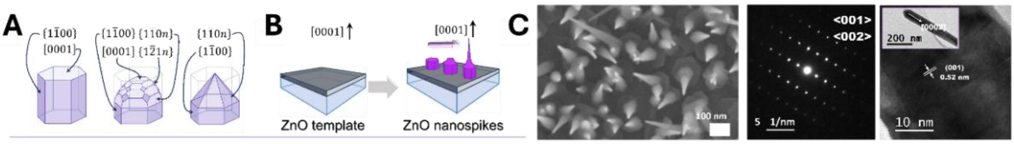

Fig. 1. A) Exposed families of planes on NR with plate-like, dome-like, and pencil-like tips. B) Scheme of the tandem AACVD process to form ZnO coatings with aligned NSPs. C) SEM images showing the presence of ZnO NRs film coatings with a concave apex tip, forming ZnO NSP coatings; and HRTEM images showing the diffraction patter of ZnO NSP film coatings.

Beyond their structural and optical advantages, these ZnO nanostructures exhibit remarkable antibacterial activity against *E. coli* K12, demonstrating superior bactericidal effects over conventional ZnO coatings (**Fig. 2**). This enhancement stems from a dual-action mechanism: mechanical membrane disruption by the spiky terminations and amplified photocatalytic activity under UVA illumination.

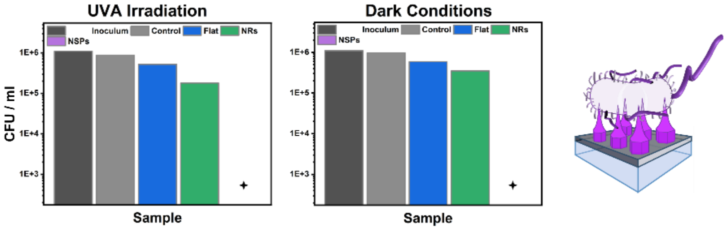

Fig. 2. Viable counts of bacteria after exposure to UVA light and to the dark. ✦ indicates that the viable count was below the detection limit of 100 CFU/ml.

Our findings position AACVD as a scalable and versatile platform for the fabrication of next-generation ZnO-based coatings, unlocking new possibilities for self-cleaning surfaces, antimicrobial applications, and advanced photovoltaics. This work paves the way for the tailored design of ZnO nanostructures with enhanced functionality, setting a new benchmark in the field.

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Acknowledgements

Authors acknowledge the financial support of the Spanish Ministry of Science and Innovation and the Spanish State Research Agency (MCIN/AEI/10.13039/501100011033) through the project POLLUTWIN (TED2021-129162B-C21) and the European Union (NextGenerationEU/PRTR). C. S.-V. would like to thank the Regional Government of Madrid for financial support through Programa de Atracción de Talento "César Nombela" 2023 (2023-T1/ECO-29048).

OC-17

Transient IR measurements as a tool for understanding photoactive materials: what have we learned from studying the photocatalytic Metal Organic Framework (MOF) MIP177?

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Developing of new, highly efficient, photocatalytic materials depends to large extent on better understanding of physical and chemical phenomena occurring right after photon absorption. Here we discuss the use of transient IR spectroscopy, operating a “Step-Scan” approach with pulsed laser excitation, for studying post-excitation processes in photoactive materials.

In the past, spectral transient changes that are sensitive to the phase of the photocatalyst and to its preparation procedure were demonstrated with carbon nitride, BiVO4, BiOCl, and hematite. Here, we report on the extension of this method to Metal Organic Frameworks (MOFs) and, in particular, MIP177(Ti). This MOF can be synthesized in forms: MIP-177(Ti)-LT (LT: Low Temperature) and MIP-177(Ti)-HT (HT: High Temperature). The MIP-177(Ti)-LT version comprises of Ti12O15 units interconnected by 3,3′,5,5′-tetracarboxydiphenylmethane (mdip) ligands and interconnecting formate groups. Upon high temperature treatment, MIP-177(Ti)-LT loses its formate groups, thus rearranging into a continuous 1-D chain of Ti_6O_9 units leading to the MIP-177(Ti)-HT. Based on this 1-D connected structure, one should expect a higher photocatalytic activity of MIP-177(Ti)-HT. Nevertheless, Hydrogen Evolution Reaction photoactivity assessment clearly indicates the opposite. Combining transient IR measurements (TRIR), TAS and DFT/TD-DFPT calculations unveils the reasons for this situation. The TRIR measurements evidence that the photoinduced electrons are located in the inorganic part, while the holes are in the mdip ligand. The longer lifetime of MIP-177(Ti)-LT is mapped onto a slower decay of the Ti-O related peaks. A reversible change in the coordination of the carboxylate groups from a bidentate to a monodentate coordination was observed only in MIP-177(Ti)-LT. Complementary DFT and TD-DFPT simulations demonstrated a higher electron delocalization on the inorganic part for MIP-177(Ti)-LT (hence, enhanced mobility and slower recombination), thus explaining its superior photocatalytic activity.

These results demonstrate, again, that transient changes in the IR spectra can serve as good descriptors for the photocatalytic activities of materials, hence may provide valuable information on these processes, in particular when the TRIR technique is integrated with other techniques.

Acknowledgements

This work was supported by the METHASOL and MOF2H2 projects, funded by The European Union under Horizon 2020 research and innovation programmes GA 101022649 and GA 101084131, respectively. The computational work was performed using HPC resources from GENCI-CINES (Grant A0160907613) and from the Très Grand Centre de Calcul (TGCC)-CEA facilities.

Unravelling the Mechanism of CO_2 Photoreduction by *Operando* Modulation Excitation IR Spectroscopy

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The photocatalytic conversion of CO_2 and H_2O to short hydrocarbons is a challenge in contemporary research, representing a convenient strategy to tackle global warming. In this regard, photoactive materials like Pt/ and, especially, $PtCu/TiO_2$ (which absorption falls into the visible range) spark great interest since a thorough optimization of their synthesis and catalytic performances would lead to converting the entire solar spectrum into solar fuels. However, the underlying reaction mechanisms of CO_2 photoconversion on these systems remain poorly understood, limiting real progresses in the field. Disclosing the connection between surface properties, structure and activity of heterogeneous photocatalyst is a challenging task, often requiring the employment of a multi-technique *operando* approach, to probe the system directly under operating conditions. Moreover, their surface reactivity often manifests itself in very subtle changes in their already intricated spectroscopic response. This makes the Modulation Excitation (ME) approach and chemometric analysis (e. g., Phase Sensitive Detection (PSD) and Multivariate Curve Resolution - Alternating Least Squares (MCR-ALS)) valuable tools to enhance sensitivity and the overall comprehension of spectroscopic data. [1, 2]

In this regard, we investigated the photocatalytic conversion of CO_2 and H_2O to hydrocarbons on Pt/ and $PtCu/TiO_2$ (PC500) by means of time-resolved IR spectroscopy coupled to GC-MS, exploiting a self-developed setup optimized to carry out sharp and effective ME experiments in *operando* conditions. We pointed out the role of carbonaceous residues (C-species) on the raw photocatalyst surface and their contribution during the photocatalytic reduction process. By post-processing the acquired IR spectra through MCR-ALS, we overcame the challenge of IR band assignment in the 1800 - 1000 cm^{-1} region, disentangling the overlapping spectral features of the raw spectra into the individual species' contributions (Figure 1). Beyond revealing the nature of the main carbonaceous species (acetates, carbonates and formates) lying on the surface of the most common photocatalysts, this work delivers an in-depth understanding of the role of the residual carbon species in photocatalysis implying an evolutive behaviour of the Pt/TiO_2 surface. With our multi-technique analysis, we demonstrated that surface contaminants in the form of carboxylates can participate in surface reactions and, by monitoring the evolution of the diverse surface species upon irradiation, we identified acetates as likely reaction intermediates in CO_2 photoconversion to hydrocarbons. [3] New ME experiments and PSD analysis (involving light/dark and gas composition modulation) are currently ongoing to enhance our mechanistic insight on CO_2 reactivity on Pt/TiO_2 and to extend the comprehension to the solar-active $PtCu/TiO_2$ system.

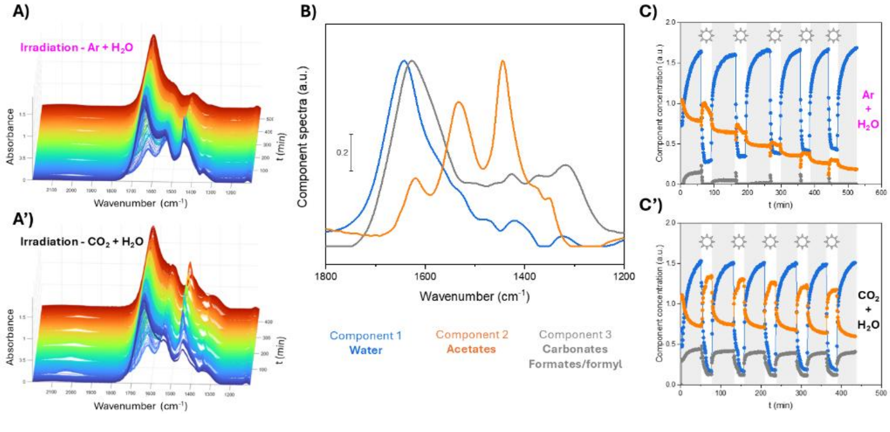

Fig. 1. IR spectra of Pt/TiO_2 collected upon light/dark cycles under (A) Ar/H_2O and (A') CO_2/H_2O flow. (B) MCR-ALS decomposition of the IR spectra. Principal components evolution upon light/dark cycles under (C) Ar/H_2O and (C') CO_2/H_2O.

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OC-19

Synthetic Protein Scaffolds for Customizable Chromophore Interactions in Energy Conversion Applications

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In nature, the photosynthetic machinery is composed of pigments placed in specific positions within protein matrices, which assist in the regulation of the embedded pigments' electronic states involved in processes such as energy absorption, transfer and conversion [1]. The *de novo* design of proteins allows the production of artificial protein scaffolds capable of performing similar functions, providing mimetics of natural Light-Harvesting Complexes (LHCs). We make use of this principle in protein maquettes containing four-alpha-helices connected via random coils, where the amino acid sequences result in water soluble structures with hydrophobic cores [2]. Due to the maquettes' robust structures, it was possible to precisely decorate them with the synthetic chromophores Zn-pheophorbide a (ZnPa) and Rhodamine 101 (R101) to activate an energy transfer path from R101 to ZnPa. In our design, ZnPa is connected to histidine residues placed inside the maquettes' hydrophobic core, and R101 is connected to one of their random coils via a cysteine residue. The obtained chromophore-protein complexes possess a very wide absorption cross-section covering a large portion of the visible spectrum as a consequence of combining both chromophores' absorption bands in the blue/red (ZnPa) and green (R101). Upon chromophore binding, we could modulate ZnPa photoluminescence: its emission efficiency increases on account of the energy transfer process and the mobility restrictions imposed by protein environment, which also ended up narrowing the emission spectrum in comparison to ZnPa free in solution. Steady-state and time-resolved fluorescence spectroscopies assisted nor only in determining the energy transfer mechanism, but also revealed new chromophore-chromophore interactions via excitonic coupling. Circular Dichroism showed that R101 gained chiral activity upon binding, and confirmed the new energy levels derived from R101 and ZnPa coupling. R101-ZnPa interactions were then probed by Stark Absorption Spectroscopy, which discriminated the new electronic states and features that account for an increment in ZnPa charge transfer character in comparison to the complex containing only ZnPa. Finally, Molecular Dynamics simulations showed that ZnPa and R101 moieties remain buried within the protein hydrophobic core, depicting an excitonic coupling of 40 cm^{-1}, in agreement with the insights obtained by the spectroscopic experiments. In summary, a bioinspired *de novo* protein scaffold was designed offering a viable alternative to produce excitonic interactions within supramolecular assemblies. Simple structural modifications in the protein amino acid sequence afforded the binding of multiple chromophores with the creation of an energy transfer pathway. Thus, our research contributes to pave the way for custom made artificial photosynthetic systems to be coupled with photonic devices such as Dye-Sensitized Solar Cells due to the maquettes' superior structuring in an eco-friendly approach that facilitates the tuning of chromophores' electronic structures and the production of electronic states capable of funnelling down the excitation energy similarly to natural photosynthetic complexes.

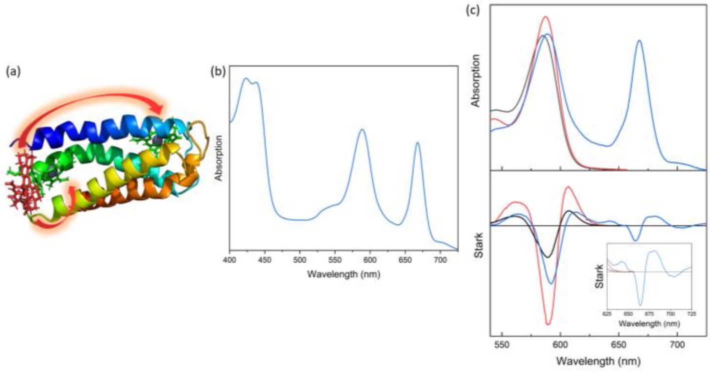

Fig. 1. (a) *De novo* chromophore-protein complex containing R101 and ZnPa (the arrows outline the energy transfer path), and (b) its absorption spectrum. (c) Absorption and Stark Spectra of R101 in buffer (black lines), complexes containing only R101 (red lines), and containing both R101 with ZnPa (blue lines).

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Acknowledgements

We thank the funding from the European Research Council under the European Union's Horizon 2020 Research and Innovation Programme (Grant agreements № 805524-Bio-Inspired_SolarH2, and 101107810-deBioLED).

OC-20

UV-visible modulation-excitation X-ray absorption spectroscopy to obtain insights in photocatalysts active species: the example of CO_2 reduction by TiO_2 supported Mo oxysulfides

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Background and motivation

In photocatalytic processes, the number of active sites is limited by light penetration and hence represents only a fraction of the total material. X-ray absorption spectroscopy (XAS) is a bulk technique, which can make it difficult to differentiate the spectator species from the active species. In this context, UV-visible modulation-excitation XAS (UV-vis-MEXAS) coupled with phase sensitive detection (PSD) has emerged as a powerful tool to highlight the contribution of active species during the photocatalytic process [1]. In this work, we implement UV-vis-MEXAS methodology using a recently developed versatile *operando* photocatalytic cell (Fig. 1.a) to rationalize the behavior of Mo oxysulfides supported on TiO_2 catalysts exhibiting appealing CO_2 photoreduction properties.

Materials and methods

Mo-based catalysts supported on TiO_2 were synthesized by a surface organometallic chemistry [2] inspired approach for 2 different Mo loadings (0.5%$_{wt}$Mo and 3%$_{wt}$Mo). Each material was sulfided at 2 different temperatures (20°C and 350°C) and thermally post-treated at 350°C under vacuum. We studied the behavior of these catalysts during the photocatalytic reduction of CO_2 by XAS at the Mo K-edge at the ROCK beamline [3], using a Xe lamp (320-720 nm) as UV-visible source. To highlight the contribution of active species during the process, UV-vis-MEXAS (coupled with PSD) was implemented at ROCK with UV-visible light pulses of 3 min (Fig. 1.b) using the *operando* photocatalytic cell and on-line gas detection (micro-GC).

Results and discussion

First, CH_4 is detected as major product when sending CO_2 and H_2O (CO_2/H_2O = 40 mol/mol) through the cell under UV-visible irradiation. Even more, the quantitative time evolutions of CH_4 production of all tested catalysts agree well with those obtained by using the photocatalytic unit commonly used at IFPEN [4] (Fig. 1.c). This validates the cell's reliability. Secondly, *operando* experiments are performed and interpreted with two levels of data analysis. 1) The evolution of the Mo K-edge XAS spectra throughout the photocatalytic test allows to correlate the progressive evolution of Mo species (slight oxidation and/or local order modifications) with the deactivation of the photocatalysts. We propose a reaction mechanism derived from these data. 2) The demodulation signals (resulting from the PSD treatment), featuring only active Mo species, reveal that the nanostructure and composition of the Mo species formed highly impact the photoactivity of the materials. Mo oxysulfides nanoclusters are active species while MoS_2 slabs are inactive and even detrimental to the photoactivity. This study simultaneously reveals how to tune the photoactivity by controlling the Mo loading and sulfidation temperature.

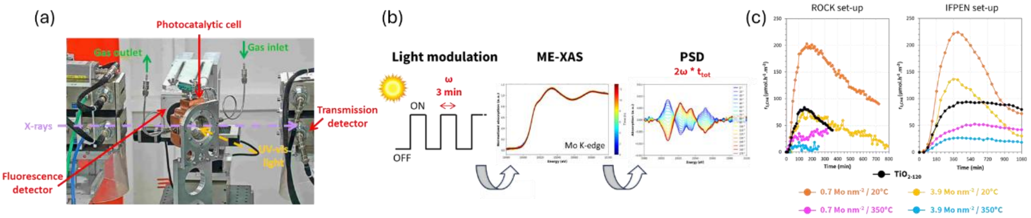

Fig. 1. (a) Newly developed operando photocatalytic cell. (b) UV-vis ME-XAS coupled with PSD methodology. (c) CH_4 production rate evolution with time for 5 different photocatalysts compared on the ROCK and IFPEN set-ups.

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OC-21

Unraveling the Role of Cobalt in Photoelectrochemical Oxygen Evolution at Fe_2O_3-CoPi Photoelectrodes via Time-Resolved X-ray Absorption Spectroscopy

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Hematite (α-Fe_2O_3) is a promising photoanode material for solar-driven water splitting due to its chemical stability and suitable bandgap. However, its performance is hindered by poor charge transport and sluggish oxygen evolution reaction (OER) kinetics. Cobalt phosphate (CoPi) has been employed as a co-catalyst to enhance the activity of Fe_2O_3, yet the mechanistic role of cobalt in this enhancement remains elusive. Three primary roles of Co have been proposed in the literature - (1) as a hole accumulator, improving charge separation[1], (2) as a direct participant in the oxygen evolution reaction (OER) by forming Co(IV) intermediates at the cobalt oxyhydroxide surface[2], and (3)enhancing light absorption, with its oxides formed during OER exhibiting visible-light absorption and serving as active catalytic sites for OER[3]. In order to understand the different roles played by Co in photoelectrochemical OER, we use time-resolved X-ray absorption spectroscopy (XAS) at the Co K-edge (Fig 1(a)-(c)) to probe the electronic and structural dynamics of Fe_2O_3-CoPi photoelectrodes under photoelectrochemical conditions. Large series of XAS spectra were analyzed as described previously[4]. We also performed measurements of optical absorption changes induced by light modulation (Fig. 1d) and looked at the hole accumulation, combining these data with photocurrent measurements using the method proposed in[5].

Steady-state XAS spectra at the Co K-edge reveal a shift in the Co oxidation state as the applied potential gets closer to OER conditions, indicating the formation of higher Co oxidation intermediates, mostly Co(III). When the light source is modulated, time-resolved difference XAS spectra show distinct spectral changes at the Co K-edge, suggesting the reversible oxidation of Co species at photoelectrochemical conditions due to the accumulation of holes from Co(II) to Co(III) (Fig.1b). We measured the kinetics (Fig. 1c) of hole recombination/consumption at the Co centers for the same system using time-resolved XAS by selecting energies near the absorption edge in the range 7.70 to 7.77 keV, maximizing sensitivity to oxidation state changes. From the comparison of these data with those obtained using optical probe (Fig. 1d) the contribution of hole accumulation at the Co centers was clarified. To further understand the involvement of Co atoms as catalytic centers, the time-resolved XAS spectra were measured for two different applied potentials corresponding to the oxidation and reduction peaks observed in the cyclic voltammogram.

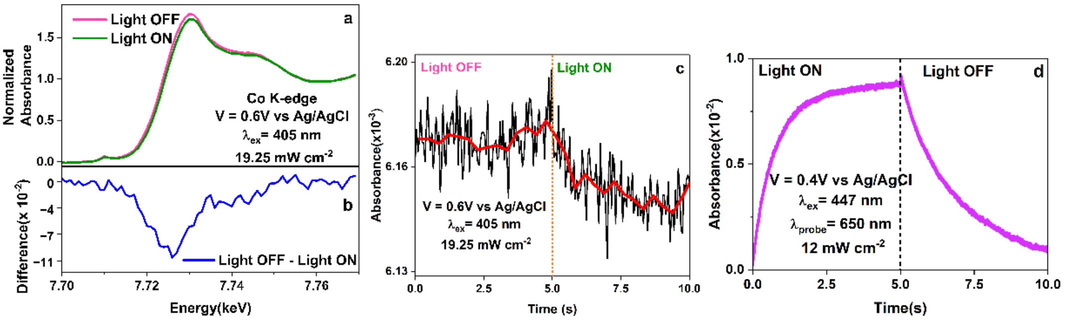

Fig. 1. (a)Difference light ON-OFF XAS spectra, (b)Steady-state Co K-edge Light OFF and Light ON XAS spectra and (c) Kinetics for time-resolved XAS; (d)Kinetics for photoinduced absorption

Our findings provide a deeper understanding of the cooperative interactions between Fe_2O_3 and CoPi, potentially guiding the rational design of more efficient photoelectrodes for solar-driven water splitting.

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Acknowledgements

We would like to thank the ESRF for providing beamtime at BM23 and the beamline scientist, Kirill Lomachenko, for his support.

OC-22

Automation of a photoelectrocatalytic wastewater treatment system for the inactivation of antibiotic resistant *E. coli*

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Photoelectrocatalysis (Electrochemically assisted photocatalysis) has been reported for the degradation of challenging pollutants in water and the inactivation of pathogenic microorganisms. With PEC, a semiconducting electrode is used either as the anode or cathode. More commonly, an n-type photoanode is used for the generation of reactive oxygen species and an applied external electrical bias is used to drive photogenerated electrons to the counter electrode to avoid recombination of charge carriers and improve process efficiency over photocatalysis alone. Furthermore, the spatial separation of the oxidation and reduction sites reduces losses due to surface recombination reactions [1].

Intensive research has been applied to photoelectrocatalysis (PEC) for water/wastewater treatment; however, the scale-up and automation of these systems hasn't been examined. For any AOP or degradative process, there must be some means of control to ensure that either target disinfection levels are achieved or that the residence time is sufficient to degrade any potentially toxic intermediates.

In this work, a PEC system has been scaled up to 1 m length with an irradiated volume of 0.85 L. The photoanode was titanium mesh coated with titanium dioxide nanotubes (TiNT) formed by anodisation. Three meshes are overlayed and combined to maximise photon absorption, and a stainless steel 316 rod (5 mm diameter) was placed in the centre of the reactor as the counter electrode. A compound parabolic collector (CPC) was used to increase the reflection of irradiation from the source (UVA lamp under lab conditions) around the circumference of the tube. The photocurrent was used to control the process by measurement of total charged passed. An Arduino controller was used to control and power supply, solenoid valves and pump to operate in sequential batch mode. The reactor was tested for the efficiency of inactivation of antibiotic resistant *E.coli* in simulated wastewater effluent. Peroxymonosulfate was added at 0.3 mM to enhance the efficiency of disinfection. When the system was operated in an automated mode it achieved a >5 log reduction in antibiotic resistance *E. coli* in synthetic wastewater.

While more work is needed on scale up of photoelectrocatalytic reactors, this work is evidence that the photocurrent can be used to provide some level of feedback control in the process efficiency.

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Acknowledgements

European Union's Horizon 2020 research and innovation programme under grant agreement No 820718 (PANIWATER). Ulster University School of Engineering Workshop: Gary Finley for CNC machining, Simon Reford for cutting and bending of titanium mesh & polished aluminium. Dr Chiara Salaris, Ulster University, School of Bulit Environment, for the use of a furnace for annealing the titanium nanotubes mesh.

Reactor design for photocatalytic water-splitting pilot plant using hybrid artificial and natural light

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Using solar power to produce hydrogen via photocatalytic water-splitting is often touted as a promising decarbonization route, but most studies have only been conducted on lab scale, and the dearth of large-scale studies is a barrier towards wider industrial adoption. Addressing this issue of scalability for the photocatalysis process requires further investigation into material synthesis and real-life demonstrations.

In this study, we demonstrate a pilot scale plant, which uses a COF-gC_3N_4 catalyst that has been synthesized on tens of grams-scale levels [1]. Initially, we conducted lab scale experiments to optimize reaction conditions and guide the pilot plant design. To allow for continuous hydrogen production, we designed a helical shaped photoreactor that allows both natural sunlight and artificial light (UV-A LEDs) to be used either separately or concurrently, using optical depth of reaction mixture as a key metric for reactor diameter.

A pilot plant, with total capacity of 4L and illuminated capacity of 1.5L, was built, which utilized compact linear Fresnel reflectors (CLFP) to allow ~5x sunlight concentration factor onto the photoreactor, with the inside of the helix containing strips of UV-A LEDs which can drive the reaction in absence of sunlight. A control panel with programmable logic control (PLC) was constructed to allow a great degree of automation to the process, with automatic data collection, temperature/flow rate/pressure monitoring, and sun tracking.

A slurry of photocatalyst, sacrificial agent (ascorbic acid) and platinum co-catalyst in water is continuously pumped through the reactor while in operation. Higher temperatures were found to be desirable for enhanced reaction rates, hence, the pilot was also designed to absorb waste heat from the LEDs to further increase hydrogen production.

Results from the pilot show a maximum production of 16 mmol/hr/g.cat of hydrogen could be achieved, which occurred during the 2nd and 3rd days of operation using the same reaction batch (which ran for consecutive 4 days), comparable to 23.4 mmol/hr/g.cat obtained at the lab scale in [2] with similar COF catalyst/ascorbic acid sacrificial agent mixture. For STH, we obtained 0.205%, which was higher than the 0.087% reported in [3], for a similar slurry-type pilot scale photoreactor. There is a capacity for hydrogen production to significantly rise pending further optimizations in reaction composition and solar tracking.

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3D-Printed Ti/TiO_2 Electrodes for Enhanced Photoelectrochemical Degradation of Emerging Microntaminants

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The widespread use of antibiotics and their persistence in aquatic environments have raised increasing concerns due to the emergence of antibiotic-resistant bacteria and potential risks to ecosystems and human health. Antibiotics are frequently detected in wastewater treatment plant (WWTP) effluents at concentrations ranging from ng L^{-1} to µg L^{-1}, and conventional treatments are often insufficient to remove these micropollutants. Developing efficient, cost-effective technologies for their removal is therefore essential [1].

This work investigates the application of Ti/TiO_2 electrodes fabricated by additive manufacturing for the photoelectrochemical (PEC) degradation of antibiotics in wastewater. Unlike traditional planar electrodes, additively manufactured 3D-electrodes offer enhanced mass transport properties and tailored surface architectures, potentially improving treatment efficiency. High costs limit conventional materials such as boron-doped diamond (BDD), whereas Ti/TiO_2 composites present a promising alternative for scalable applications [2].

Photoelectrochemical degradation experiments were performed in 250 mL Pyrex glass batch reactors illuminated with UVA-light, using synthetic wastewater simulating WWTP effluents doped with 10 µg L^{-1} of a mixed antibiotic solution. The antibiotic mixture comprised compounds from the macrolide, fluoroquinolone, quinolone, tetracycline, sulphonamide, lincosamide, penicillin, and nitroimidazole families, selected based on their inclusion in the EU Watch List (EU 2022/1307) of substances of concern due to their persistence and potential environmental risks [3].

The electrochemical characterization of the electrodes was carried out by linear sweep voltammetry (LSV) under dark and illuminated conditions (solar simulator, 1 sun). LSV was conducted from -0.5 V to +1 V vs Ag/AgCl at a scan rate of 5 mV s^{-1}. Based on the photoresponse and onset potentials observed in the LSV curves, appropriate potentials were selected for chronoamperometric experiments aimed at maximizing photocatalytic degradation.

The analytical methods for antibiotic detection and quantification were carefully optimized, given the challenge of working at such low concentrations. Sample preparation involved solid-phase extraction (SPE) to achieve high recovery rates and high preconcentration factors. Analysis and quantification were performed by ultra-high-performance liquid chromatography coupled to tandem mass spectrometry ((U)HPLC-MS/MS) with an electrospray ionization source operating in positive mode, using the multiple reaction monitoring (MRM) method.

Preliminary results reveal the necessity to perform various control experiments to isolate the effects of adsorption and photolysis. Notably, at concentrations below 10 ppb, antibiotics from the macrolide or quinolone family exhibited some adsorption over time onto the Pyrex reactor walls, while tetracyclines and fluoroquinolones demonstrated substantial photo-induced degradation under UVA-light, confirming their high photosensitivity.

The preliminary findings have revealed encouraging results for the photoelectrochemical process using additively manufactured Ti/TiO_2 electrodes as an effective strategy for removing complex, persistent, and anthropogenically derived contaminants, such as antibiotics, from wastewater. The ability to tailor electrode architectures through 3D printing—by optimizing features such as surface area, porosity, and light absorption pathways—provides a powerful approach to enhance charge transfer efficiency, light harvesting, and overall photoelectrocatalytic performance in the removal of emerging microcontaminants.

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Acknowledgements

This work has received financial support from the Instituto de Investigación de Tecnologías para la Sostenibilidad (ITPS).

OC-25

Innovative strategy for in situ and quick photocatalytic measurements on asphalt road surfaces under real-world exposure conditions

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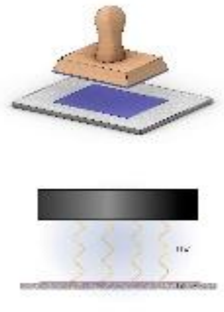
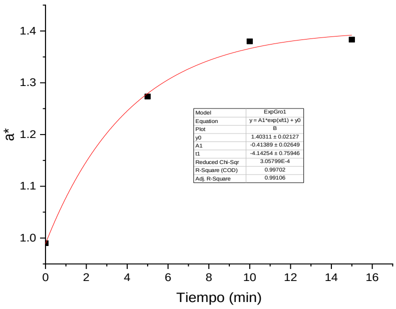
This work presents a novel method for measuring in situ photocatalytic activity under real-world exposure conditions of functionalized surfaces. This method is based on the use of photocatalytic activity indicator inks given in [1] having developed a protocol to conveniently measure –rapidly and in situ- the activity of the photocatalytic materials. The procedure is based on monitoring the photodegradation of a color indicator sensitive to redox reactions driven by the photoactivated material [2], with integrated analysis of the results. The device triggers the photocatalytic process using its own adjustable light source and detects photocatalytic efficiency through the gradual color change in the probe, providing a semi-quantitative efficiency value.

This specific study has focused on in situ activity measurements by the aforementioned method in 33 streets in Madrid, on the asphalt road surfaces, previously treated with a photocatalytic emulsion. A total amount of 216 measurements were taken at the time of product application and at two different exposure times, while exposed to road traffic. Additionally, laboratory measurements were performed on extracted samples [3] according to the standard method ISO 22197-1 – Nitrogen oxides air purification. The results obtained through both methods were correlated, demonstrating that the in situ measurement method, based on indicator inks and the associated adjustments, provides an adequate estimation of photocatalytic activity in real-world environments. Both the proposed and standardized tests showed a clear decrease in photocatalytic efficiency over time. A significant loss of photocatalytic activity occurs as a function of exposure time, with approximately 60% of the streets showing no detectable activity using the ink method, even when measuring in areas that initially presented the highest amount of photocatalytic product.





Model	ExpGro1
Equation	y = A1*exp(x/t1) + y0
Plot	B
y0	1.40311 ± 0.02127
A1	-0.41389 ± 0.02649
t1	-4.14254 ± 0.75946
Reduced Chi-Sqr	3.05799E-4
R-Square (COD)	0.99702
Adj. R-Square	0.99106

Time (min)

Fig. 1. Schematic view of the measurement process.

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Acknowledgements
The authors are grateful to CEMOSA and SOCOTEC for their support in the logistics of the in situ measurements.

OC-26

Real-Scale Evaluation of Photocatalytic Pavement Performance for NOx Abatement in Urban Environments

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Over the past decades, extensive research has been conducted to assess the photocatalytic abatement of NO_X under real-scale conditions. Initial laboratory studies demonstrated the ability of TiO_2-based materials to oxidize nitrogen oxides under controlled environments [1]. These encouraging results led to various field trials, such as the use of photocatalytic pavements and coatings in urban areas (e.g. Bergamo, Rome, Madrid), with reported NO_X reductions ranging from 20% to 80% depending on design and environmental conditions. However, other large-scale initiatives—including Life PhotoPAQ, MINOx-STREET, EQUINOX and PHOTOSCALING—highlighted the complexity of isolating a measurable photocatalytic impact on ambient NO_X concentrations under real urban conditions, due to high dispersion, meteorological variability, and low signal-to-noise ratios in open environments. These findings underline the limitations of previous evaluation approaches and the need for robust, standardized methods for in situ assessment of photocatalytic performance [1].

This study introduces an improved methodology for evaluating photocatalytic performance under real urban conditions. Advancements include long-term monitoring, normalization procedures, and the use of sensor technologies with high spatial and temporal resolution, collecting data every ten minutes over extended periods. Although the positive results may partly reflect improved photocatalytic formulations, the specific contribution of material evolution was not evaluated in this work.

The study was conducted on a high-traffic section of the C-31 road in Barcelona (Spain), where a photocatalytic surface treatment was applied to selected segments. Monitoring was carried out simultaneously in both treated and untreated reference sections using sensors validated against a reference air quality monitoring station. Data were collected from August 2023 to January 2025. Environmental variables such as solar radiation, precipitation, temperature, and traffic density were also considered to contextualize and normalize the results. The findings show a reduction in NO and particularly NO_2 concentrations in the treated section compared to the reference. Analysis of average daily profiles revealed a decrease in NO and NO_2 concentrations during daylight hours in the treated section, consistent with the presence of solar radiation and the activation of the photocatalytic process. In contrast, PM concentrations—expected not to be directly affected by the treatment—showed no significant differences between sections, supporting the specificity of the observed effect on NO_X. A temporal variation in treatment effectiveness was observed, with an initial decline followed by a recovery phase, likely linked to the cleaning effect of rainfall after an extended dry period. Monthly trend analysis suggests that photocatalytic activity contributed to average NO_2 reductions between 15–25% during periods with regular rainfall and sufficient solar radiation. The results demonstrate the applicability of the proposed methodology for assessing photocatalytic performance in real environments, as well as the potential of these treatments as complementary strategies for improving urban air quality. However, future work should consider evaluating the long-term evolution of material activity and its relation to environmental exposure.

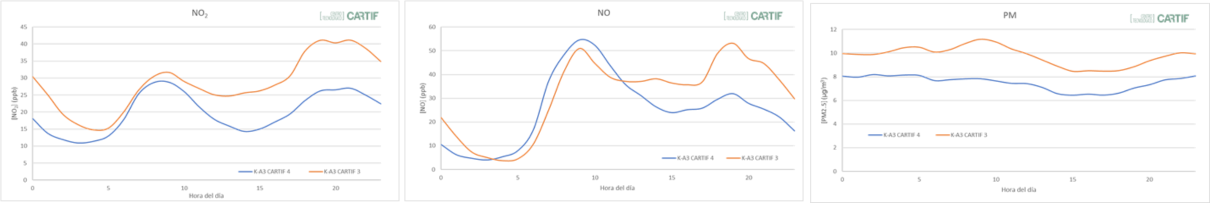

Fig. 1. Average daily profiles of NO_2, NO, and PM concentrations in photocatalytically treated (CARTIF 4) and untreated (CARTIF 3) road sections during the full monitoring period.

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Acknowledgments

This study is partially related and funded with the K-HEALTHinAIR project, Grant Agreement n° 101057693, under a European Union's Call on Environment and Health (HORIZON-HLTH-2021-ENVHLTH-02).

OC-27

Cavitation-assisted TiO_2 photocatalysis for removal of bisphenols present in water at environmental concentrations

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As a quaternary treatment, advanced oxidation processes (AOPs) are a well-established technology for treating polluted aquatic systems due to their versatility, non-selective oxidation, and ability to work synergistically with other treatment methods. For instance, they can be integrated with biological, physical, or chemical processes to enhance overall treatment efficiency. When considering heterogeneous photocatalysis as an example of AOP, solar-powered immobilised catalyst is essential for sustainable water purification [1]. Combinations of various AOPs appear to be even more effective and a promising way forward to meeting new demands and regulations.

In this research, we investigated the degradation of bisphenol A (BPA), bisphenol S (BPS), bisphenol F (BPF), bisphenol AF (BPAF), and tetramethyl bisphenol F (TMBPF) in water at two concentrations levels: 200 ng/L and 1000 ng/L, using immobilised TiO_2 in photocatalysis coupled with hydrodynamic cavitation. The experiments were carried out using two matrices; tap water (Fig. 1) and wastewater from the local municipal wastewater treatment plant. The P-25 TiO_2 photocatalyst was immobilised onto foamed alumina monoliths effectively via the sol-gel route [2] and shown to be suitable for long-term use even in wastewater. Analysis of the spent catalyst revealed no changes to its structure, only carbon and Ca deposits were detected. As expected, the degradation of bisphenols took place much more readily in clean water than in wastewater, most likely due to other organic matter present in addition to the bisphenols [3, 4]. The current study shows an important improvement in the applicability of the two methods for treating polluted water bodies.

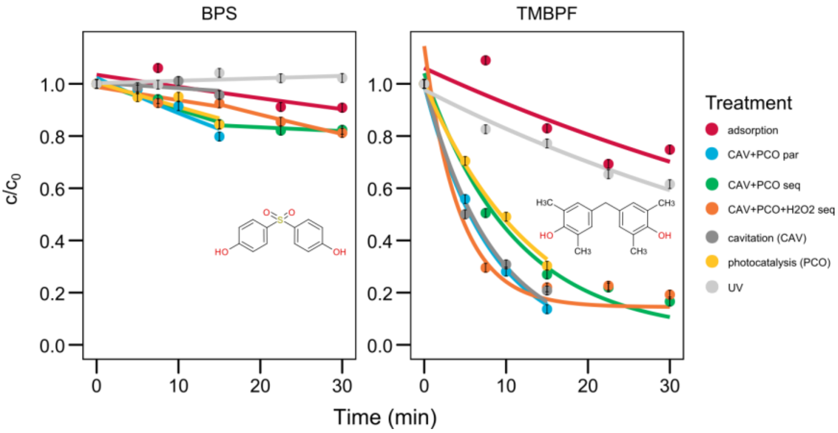

Fig. 1. Removal of two bisphenols (borderline cases) using selected treatment setups for tap water. The data were fitted to the non-linear form of the first-order reaction rate.

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Acknowledgements

This work was financially supported by the Slovenian Research and Innovation Agency through the projects No. L7_1848, No. J2-4444, No. J2-4441, N2-0310 and N2-0381, as well as core programs No. P1-0134 and No. P1-0143. We acknowledge NETPORE COST Action CA20126 for its support.

OC-28

Mechanistic Insights into PFOA Photodegradation: Effects of Catalyst composition, Surface Modifications, and Irradiation Wavelength

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Over the past several decades, poly- and per-fluoroalkyl substances (PFAS) have emerged as a significant environmental concern due to their widespread industrial and consumer applications. These persistent pollutants have been detected in humans, animals, and ecosystems, raising alarms over their toxicity and potential carcinogenic effects [1]. The key challenge in addressing PFAS contamination lies in their exceptional chemical stability, primarily due to the high bond energy of the C–F bond, which makes conventional water and wastewater treatments ineffective [2]. As a result, there is an urgent need for innovative degradation strategies. Among emerging approaches, photocatalysis has gained attention as a sustainable method driven by solar energy, offering a promising route for PFAS breakdown. However, despite recent advances, the degradation mechanisms and efficiency of photocatalysis for PFAS removal remain largely unexplored, making it a rapidly evolving research area with significant knowledge gaps [3].

Unlike conventional photocatalytic studies that primarily focus on oxygen-rich environments, this work investigates the degradation of perfluorooctanoic acid (PFOA) under anoxic conditions, offering new insights into alternative reaction mechanisms and potential electron transfer pathways. To enhance photocatalytic performance, various combinations of UVC or UVA light with TiO_2 or In_2O_3 nanopowders, modified with Au or Ag nanoparticles, were explored. Additionally, a UVC/KI system was tested as a benchmark for comparison [4].

Both TiO_2- and In_2O_3-based catalysts exhibited significant PFOA adsorption in dark conditions, underscoring the importance of distinguishing between mere adsorption and true photocatalytic degradation. To accurately assess reactivity, the identification and quantification of reaction products, such as shorter chain perfluoroalkyl carboxylic acids, were crucial. The TiO_2-based catalysts demonstrated higher activity under UVA irradiation, while the In_2O_3-based catalysts were more effective under UVC light (Fig. 1). Notably, the UVC/In_2O_3 systems achieved the fastest PFOA removal, outperforming both the UVA/TiO_2 and UVC/KI systems. A reaction mechanism is proposed based on the observed reactivity and photocatalyst properties.

These findings elucidate how photocatalyst composition, light wavelength, and surface modifications influence PFOA degradation under anoxic conditions, providing a deeper understanding for the rational design of advanced PFAS remediation technologies.

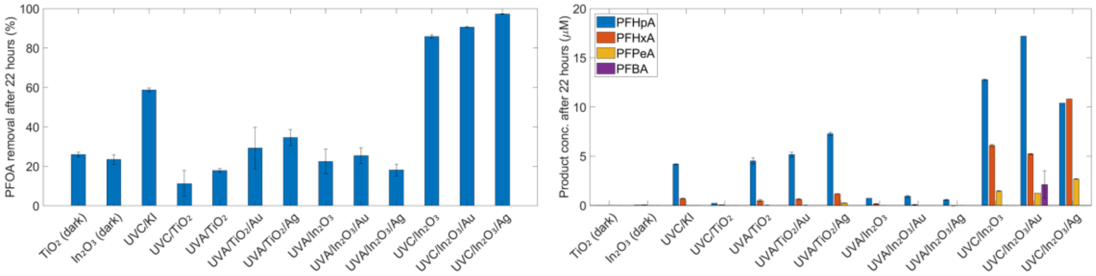

Fig. 1. PFOA removal (left) and distribution of degradation products (right) in different photocatalytic systems.

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Acknowledgements

The authors acknowledge Flanders Innovation & Entrepreneurship - VLAIO, Catalisti, and all the partners of the Cluster SBO project 'FF-PFAS' for their financial support.

OC-29

Solar photocatalytic oxidation and heterogeneous ozonation of p-chlorophenol and sunset yellow in a CPC reactor using iron-supported polyurethane foam and pumice beds

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The increasing contamination of water bodies due to the presence of emerging pollutants in industrial effluents—many of which exhibit high resistance to conventional wastewater treatment methods—has underscored the urgent need for more efficient removal strategies for recalcitrant contaminants. Advanced oxidation processes (AOPs) have emerged as promising alternatives, demonstrating effectiveness in degrading complex compounds such as dyes and pharmaceutical substances.

This study investigates the application of AOPs for the degradation of two persistent industrial pollutants, 4-chlorophenol and Sunset Yellow, using photolytic and heterogeneous photocatalytic systems in compound parabolic collector (CPC) reactors. Heterogeneous photocatalysis was performed using fixed beds of iron oxides supported on natural pumice stone and commercial polyurethane foam, with a particle size range of 0.71–1.4 mm. The catalytic beds were synthesized via co-precipitation of Fe(II) and Fe(III) in an alkaline medium, based on the protocol proposed by Çifçi et al. (2021) [1], with certain modifications. Characterization of the catalysts was conducted using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD), among other techniques, to assess their catalytic activity as well as surface properties.

The evaluated technologies included ozonation, Fenton, and photo-Fenton, as well as combinations such as ozonation/UV and ozonation/H2O2. Among the catalytic techniques, the photo-Fenton process was the most effective in contaminant degradation. In this process, the pumice stone-based catalyst exhibited higher activity in contaminant degradation compared to the polyurethane foam catalyst, with degradation percentages of 45.1% for 4-chlorophenol and 55.4% for Sunset Yellow. Regarding chemical oxygen demand (COD) removal, catalytic techniques, especially the photo-Fenton process, were the most effective, achieving maximum removal percentages of 94.1% for 4-chlorophenol on the pumice stone bed and 96.3% for Sunset Yellow on the polyurethane foam bed.

These results demonstrate the potential of advanced oxidation technologies, particularly the photo-Fenton process, as a promising strategy for the removal of recalcitrant contaminants from industrial wastewater, paving the way for future applications and optimizations of these processes in effluent treatment systems.

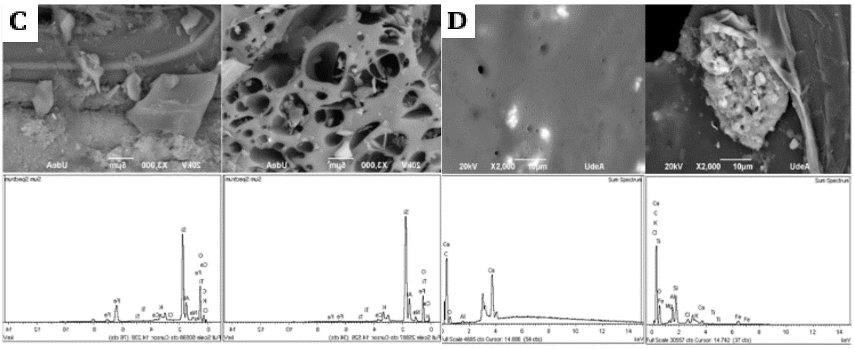

Fig. 1. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) techniques on C) natural pumice, photograph at 2000x magnification and sum spectra of the impregnated (left) and unimpregnated (right) pumice and D) commercial polyurethane foam, Photograph at 3000x magnification and sum spectra of the unimpregnated (left) and impregnated (right) polyurethane foam.

In Figure C right, a porous and uniform surface can be seen. The micrograph of the impregnated pumice reveals a notable morphological change after the incorporation of iron oxides, where the surface no longer presents the same porosity and uniformity, but appears compact. For the unimpregnated foam, a compact and uniform surface is observed, with some pores and white areas. With the addition of iron oxides, the morphological and surface properties of the foam changed significantly. The surface went from being compact and uniform to presenting clusters of particles.

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Photocatalytic Degradation of PFOA: The Role of Adsorption, Repeatability, and Toxicity Outcomes

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Per- and polyfluoroalkyl substances (PFAS), such as perfluorooctanoic acid (PFOA), are widely recognized for their exceptional chemical stability and environmental persistence, stemming from their strong carbon–fluorine bonds. Among advanced remediation methods, photocatalysis using modified titanium dioxide (TiO_2)-based materials offers promising degradation capabilities. However, the efficiency of these systems is often overestimated due to unaccounted adsorption of degradation products—particularly fluoride ions—onto catalyst surfaces and reactor walls. These effects become especially problematic at low, environmentally relevant PFAS concentrations, where even minimal adsorption can skew performance assessments.

In this study, PFOA degradation was evaluated using a variety of TiO_2-based photocatalysts under UV light. Defluorination remained minimal at low PFOA concentrations (<0.5%), while at higher concentrations it increased to 37 ± 3%, with total degradation exceeding 90%. Sodium fluoride control experiments confirmed that up to 82 ± 3% of released fluoride could be lost via adsorption, further complicating defluorination assessment. Reactor material was also a factor: PTFE exhibited the lowest fluoride interaction, whereas glass showed the highest, emphasizing the need to consider surface material properties such as polarity and energy.

Two photocatalytically treated samples were further analysed. In terms of PFOA transformation, S1 showed 36.7% chain-shortening and 2% defluorination, while S2 achieved 60% chain-shortening and 6.2% defluorination. These findings illustrate how deeper structural degradation can occur even when fluoride release is limited—likely due to strong surface retention of fluorinated intermediates. However, the modest defluorination efficiencies reinforce the critical role of surface phenomena in evaluating degradation completeness.

Repeatability across identical experimental conditions was also a concern. Variability in catalyst surface properties and subtle environmental differences resulted in inconsistent degradation and defluorination metrics, raising questions about the comparability and reproducibility of such studies.

To complement chemical analysis, toxicity assessments using Vibrio fischeri revealed that untreated PFOA exhibited 47% maximal bioluminescence inhibition, with EC10 and EC20 values of 7.9 and 14.9 mg/L. Post-treatment, S1 and S2 showed reduced toxicity, with maximal inhibitions of 35% and 28%, and EC20 values increasing to 23.5 and 22.8 mg/L, respectively. These results suggest that even partial degradation leads to significant detoxification, reinforcing the environmental relevance of photocatalytic remediation.

Altogether, these results underscore the importance of integrating adsorption behaviour, reproducibility analysis, and toxicity metrics alongside standard degradation and defluorination measurements to enable robust assessment of PFAS photocatalytic treatment systems.

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Acknowledgements

Funding for this research is provided by the Slovenian Research Agency (ARIS) within the framework of research program groups P1–0134, P1- 0418 and the project J2-4444 (SoAPperF).

OC-31

Exploring the Dual Photoelectrochemical Activity of Carbon Nitride Films Grown by Electrophoretic Deposition

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The increasing demand for sustainable water treatment technologies calls for novel, efficient, and low-cost photoelectrode materials. Carbon nitride (CN), a polymeric semiconductor composed of Earth-abundant elements, has gained attention due to its tunable band gap, chemical stability, and potential for photoelectrochemical (PEC) applications [1,2]. In this work, CN films were synthesized by a green electrophoretic deposition (EPD) method onto fluorine-doped tin oxide (FTO), using guanidine chloride and urea as precursors. Films of different thicknesses were obtained by varying the EPD time (from 0.5 to 10 min) at constant voltages of 20 V and 50 V, followed by annealing at 300 °C.

Optical film characterization was performed through Tauc plots to determine their band gap and energy band diagrams. PEC performance was evaluated under simulated solar light (AM1.5G, 100 mW·cm^{-2}) by linear sweep voltammetry (LSV), photocurrent transients, and open-circuit potential (OCP) measurements. The effect of illumination side (electrode-electrolyte -EE, front- or substrate-electrode -SE, back-) was also assessed. The OCP results (Fig. 1A) revealed a predominantly cathodic behavior (p-type), which could be modulated by the applied polarization, as confirmed by LSV (Fig. 1B). The ambivalent photoresponse suggests the material can behave either as a photoanode or photocathode depending on the applied potential. According to the chronoamperometry (Fig. 1C-D), stable anodic and cathodic photocurrents were achieved depending on the bias, demonstrating a dual behavior. This dual behavior paves the way for electrophoretically deposited CN films' environmental applications in advanced oxidation processes (e.g., water splitting and pollutant removal).

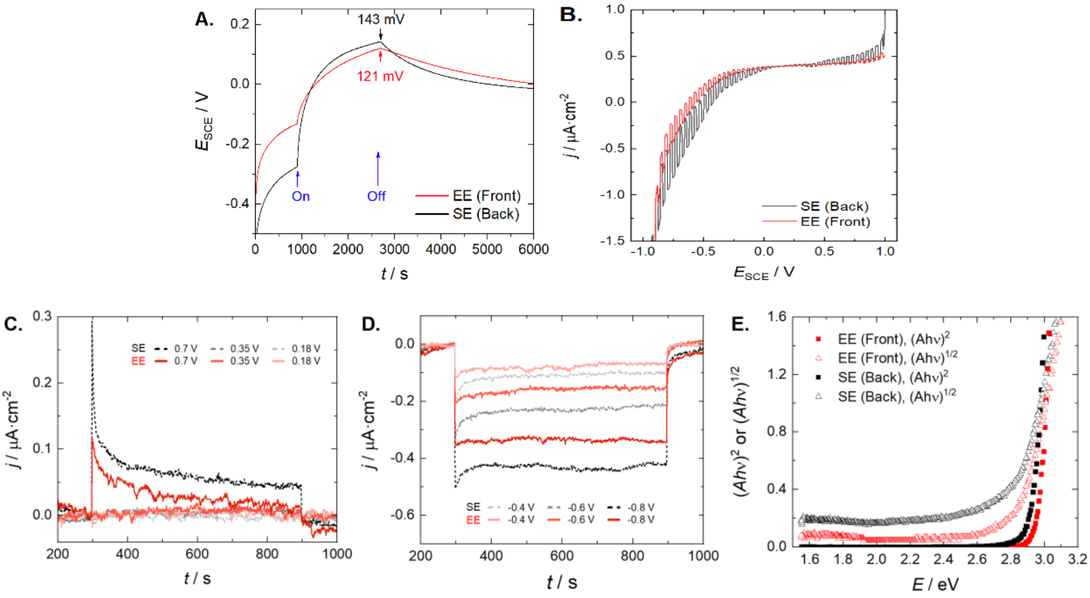

Fig. 1. Photoelectrochemical characterization of electrophoretic CN films (1 min, 50 V). (A) Open-circuit potential (OCP) measurements under light/dark cycles; (B) Linear sweep voltammetry (LSV) curves; (C) Chronoamperometry at anodic and (D) cathodic potentials; (E) Tauc plot derived from optical characterization.

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Acknowledgements

This work has been supported by Project VALPIG4FOOD (TED2021-129595B-I00) and Consolidación Investigadora 2022 (CNS2022-136107), both funded by the Spanish Ministry of Science, Innovation and Universities and the European Union's NextGenerationEU. This work has received financial support from the Instituto de Investigación de Tecnologías para la Sostenibilidad (ITPS).

Ceria nanostructures as support for metallic clusters: optical properties and catalytic activity

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Ceria is a catalyst that exhibits high oxygen storage capacity (OSC), which enables it to undergo rapid and repetitive redox cycles. This property is associated with the ease of creation, regeneration, and diffusion of oxygen vacancies, particularly on the surface of this oxide [1,2]. These properties can be modified by introducing defects, such as dopant insertion, and thermal treatments under low oxygen pressure, inducing the formation of Ce^{3+}/Ce^{4+} redox pairs and oxygen vacancies (VO). Ceria is applied in petroleum cracking processes, three-way catalysts, photo catalysis, fuel cells, and CO oxidation and CO_2 reduction reactions [1] and it is also employed as support in oxidation reactions, with improved efficiency owing to the metal-support interactions. Several studies have shown that ceria nanoparticles decorated with noble metal nanoparticles (Au, Ag) exhibit an increased concentration of Ce^{3+} and oxygen vacancies, which are crucial for these applications. The photocatalytic mechanism in the presence of metallic nanoparticles involves charge transfer to CeO_2, which acts as a support [3,4]. Additionally, with the use of metallic nanoparticles, visible-light photon absorption is amplified due to the surface plasmon resonance phenomenon [4], making it an efficient system for the photocatalytic degradation of dyes [5,6] and CO oxidation [7]. Beyond defect generation, the material's morphology greatly influences its catalytic activity, once the reactions occur at the molecular level on the surface/interface of solid catalysts, where reactants are adsorbed and converted into products that are later desorbed from the catalyst's surface [8]. In this regard, efforts have been made to synthesize materials with different morphologies in an attempt to control defects and improve their efficiency in catalytic reactions [9]. Thus, the synthesis of two-dimensional (2D) materials with high surface area and a high concentration of active sites on the surface presents an alternative to bulk materials. In order to evaluate the morphology effects in CeO_2 catalytic activity, ceria nanoplates, nanosheets and nanowires were synthesized and doped/impregnated with Au and Ag. For impregnated samples, TEM images showed the presence of small metallic particles. Raman spectroscopy showed an enhancement in oxygen vacancies in samples doped and impregnated with Au and Ag, and the samples were tested in a reaction model [10] for the photo plasmonic oxidation of p-aminothiophenol (PATP) through plasmonic activation of O_2 in ceria/metal interface. Our results showed an enhancement in PATP conversion to DMAB under 633 nm excitation for samples impregnated with Au and Ag nanoparticles. EPR measurements were performed in order to identify the nature of such oxygen species and the results point to the presence of superoxide species.

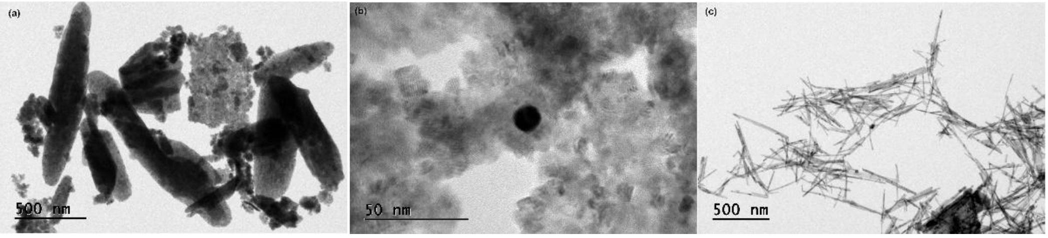

Fig. 1. TEM images of (a) ceria nanoplates, (b) Au impregnated ceria nanoplates and (c) ceria nanowires.

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Acknowledgements

This work has received financial support from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (grant number 2024/09973-6), CNPq and CAPES.

OC-33

Photocatalytic Logic Gate Behavior of Copper-Based Catalysts Driven by NIR and Visible Double-Photon Process

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Although the dynamic restructuring of metalated-Cu within metal-organic frameworks (MOFs) for photocatalytic applications has been studied recently, insights into electronic excitation remains insufficiently investigated. [1-2] To explore this, we examined the light-induced behavior of a Cu-metalated UiO-66-(COOH)2 framework (Fig. 1A) under various irradiation conditions, using complementary operando techniques. A gas-phase photocatalytic dehydrogenation of formic acid (FAc) was chosen as a model reaction under ambient conditions. For the first time, a photocatalytic logic gate behavior was observed and evidenced. The MOF remained in the OFF state under either visible (>390-720 nm) or NIR (>700 nm) irradiation but exhibited a high H2 production rate of 6.1 mmol g-1 h-1 (ON state) when both irradiations were applied (Fig. 1B). Operando FTIR and XAS analysis showed that both visible and NIR irradiations were needed for the restructuring of the metalated Cu2+ within the framework (Fig. 1B), leading to the formation of an active Cu0/Cu+ binary center for photocatalytic dehydration of formic acid. Additionally, XAS results indicated that the photoreduction of pristine Cu2+ to Cu+ and Cu0 were promoted differently under visible-light and NIR irradiation, respectively. A cascade reaction mechanism (involving alternating visible and NIR irradiation cycles) was demonstrated, where both types of photons were required for generating the active Cu0/Cu+ species and maintaining the dynamic photocatalytic redox cycle to generate H2 from FAc (Fig. 1C). This novel photocatalytic logic gate behavior was not limited to the Cu-metalated UiO-66-(COOH)2 but was also confirmed in binary Cu0/Cu2O photocatalyst used as a reference. These findings offer new insights into dual-photon-driven photocatalysis with metal-semiconductor materials and open up opportunities for designing advanced photocatalysts for efficient hydrogen production.

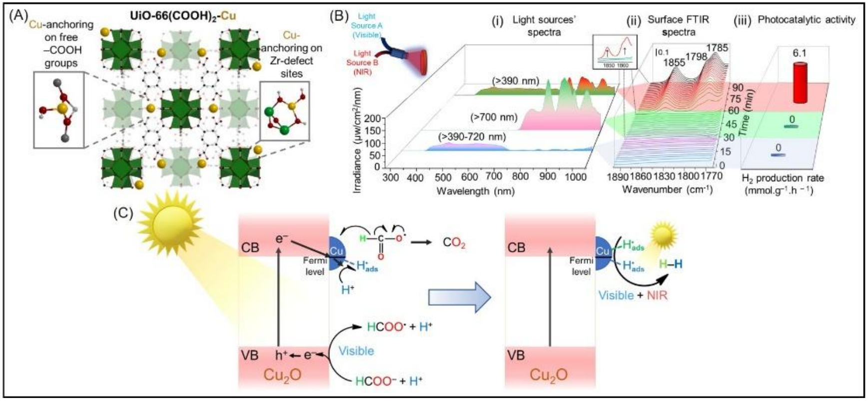

Fig. 1. (A) Structure of UiO-66-(COOH)2 MOF, highlighting the possible Cu(II)-anchoring sites, (B) (i) the irradiance spectra of light sources; inset left: the configuration of the light irradiation of the photocatalyst in a pallet form, (ii) the operando FTIR surface spectra in the anhydride region during dehydrogenation of FAc under various irradiation condition (inset: the spectra at steady state: under visible (blue), NIR (green) and visible+NIR (red) irradiations respectively), (iii) H2 production at the steady state under each particular irradiation condition. (C) Schematic illustration of the photocatalytic production of CO2 and H2 over in-situ restructured Cu^0/Cu$^+$ active centres under visible and NIR irradiations.

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Acknowledgements

The European Union under the Grant Agreement #101084131 (MOF2H2 project) is acknowledged for funding.

OC-34

Hybrid CdSe/ZnS Quantum Dots-Gold Nanoparticles Composites Assembled by Click Chemistry: Towards Affordable and Efficient Redox Photocatalysts

Vincent Maurel,[a] *Ali Dabbous,*[a] *Pierre Bauer,*[b] *Coralie Marcucci,*[a,b] *Sandy Périé,*[a,b] *Sapna Gahlot,*[a,b] *Christian Lombard,*[a] *Sylvain Caillat,*[a] *Jean-Luc Ravanat,*[a] *Jean-Marie Mouesca,*[a] *Stéphanie Kodjikian,*[b] *Aude Barbara*[b] *and Fabien Dubois*[b]

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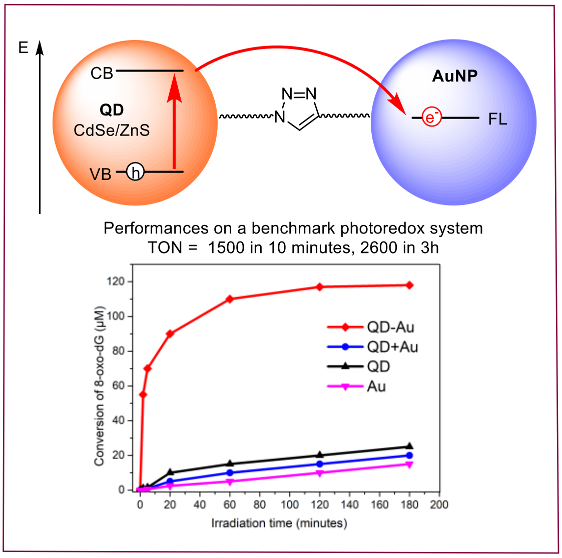

Performances on a benchmark photoredox system
TON = 1500 in 10 minutes, 2600 in 3h

A new modular, easy-to-synthesize photocatalyst was prepared by assembling colloidal CdSe/ZnS quantum dots (QD) and gold nanoparticles (AuNP) via their ligands thanks to Copper-Catalyzed Azide to Alkyne Cycloaddition (CuAAC) click chemistry. The good connection of QD and AuNP was evidenced and the size of the resulting composites was explored by combining confocal DLS and FCS [1].

The resulting composite (QD-AuNP) photocatalyst was tested with a benchmark photoredox system previously reported by our group, for which QD alone acted as photocatalyst, but with a modest Quantum Yield (QY = 0.06%) and turnover number (TON = 350 in 3 hours) due to poor charge separation [2].

After optimization, the QD-AuNP composites exhibited much improved photocatalytic performances: up to 5 times higher TON (2600 in 3 hours), and up to 24 times faster reaction in the first 10 minutes of visible irradiation [3]. Such an improvement is attributed to an efficient electron transfer from QD to AuNP in the photoexcited QD-AuNP composites, which ensures a much better charge separation than in QD alone.

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OC-35

Combining Quantum Dots with NHCs as Exciton Delocalizing Ligands for boosting their photocatalytic activity

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The use of colloidal semiconductors – Quantum Dots - as photocatalysts in oxido-reductive reactions induced by light has gradually been increasing over the past several years due to their tuneable optical and electrical properties.[1] They have a high absorption in visible light depending on their size and functionalization. Previous works in our laboratory have shown that replacing a rare metal based photocatalyst such as Ir(III) by CdSe Quantum Dots could give very similar yields but need a longer reaction time. [2] In order to reduce this reaction time, the charge recombination happening between the electron and the hole of the Quantum Dots needs to be prevented. Indeed, the more the charges can be delocalized, the slower it is for them to recombine. In this context, ligands that have an EDL effect (exciton delocalizing ligand) can be followed by UV-vis measurements through a shift of the first excitation peak and are expected to give better results in photochemical reactions. [3],[4]

In this work, we study the EDL effects of different NHCs (N-heterocyclic ligand) on several Quantum Dots and their application in light induced radical reactions useful in synthetic chemistry. We manage to form C-C, C-S and C-Se bonds from the photogenerated carbon-centred free radicals. This work is supported through DFT calculations.

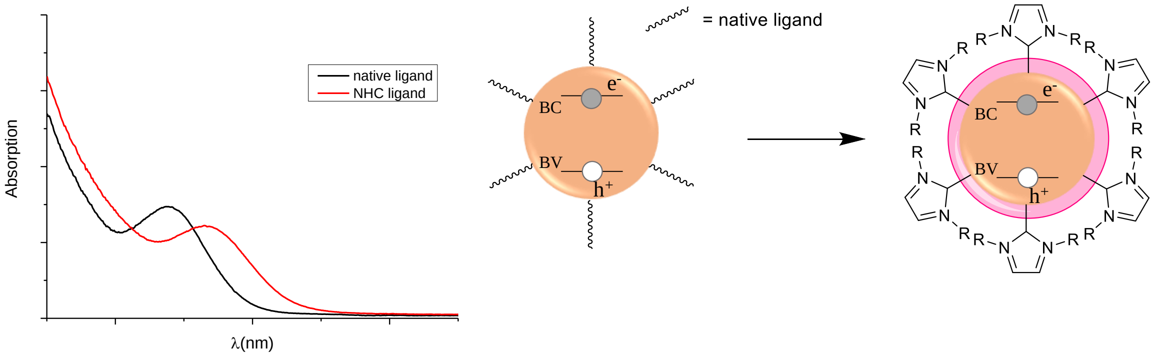

Fig. 1. Shift in UV-vis absorption measurements observable during a ligand exchange with NHC.

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Metal incorporated UiO-66(Zr)–NH_2 frameworks as effective photocatalysts in the hydrogen production

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Due to its abundance and eco-friendly nature, solar energy has been recognized as a promising alternative to address the global energy crisis and human overreliance on fossil fuels, which causes environmental pollution. Photocatalysis has emerged as an effective method for transforming solar energy into chemical energy, including producing hydrogen, using different materials like semiconductors [1, 2].

Traditional semiconductors such as TiO_2 and ZnO have been extensively studied; however, their photocatalytic activity is mostly limited to the UV region of the solar spectrum. Numerous strategies, including morphological engineering, doping, photosensitizer integration, and construction of semiconductor heterojunctions, have been employed to enhance their performance [3, 4]. Nevertheless, the search continues for photocatalysts that are both stable and efficient materials for hydrogen production.

Metal-organic frameworks (MOFs), particularly the zirconium-based UiO-66(Zr) structures, have attracted significant attention due to their chemical and thermal stability, high surface area, porosity, and structural tunability [1]. Despite these advantages, their photocatalytic activities have been hindered by inefficient photogenerated charge transfer from the excited ligands to the Zr–O clusters [1, 3].

Fortunately, UiO-66 frameworks are highly versatile and allow for easy modification - such as ligand functionalization, defect engineering, or coupling with another photo-functional component - that can significantly enhance light-responsive, charge separation, and photocatalytic activity [1]. Functionalizing UiO-66(Zr) linkers, like -$NH_{2,}$ enhances its photocatalytic performance. Improving the charge separation proficiency within the 3D network of MOF has become of significant interest [3].

The aim of this study was a synthesis of UiO-66(Zr)-NH_2 photocatalysts through solvothermal methods with the addition of different metals (Ce, Fe), aiming to create stable and efficient materials for photocatalytic hydrogen generation. The photocatalytic activity was examined in the stirred batch photoreactor using a methanol-water mixture. Structural, textural, optical, and electrical properties were systematically analyzed to establish their relationship with photocatalytic activity. The results revealed that the addition of a metal source in the photocatalyst significantly influenced the photocatalytic efficiency of hydrogen generation.

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OC-37

MOCHAs: Hybrid Organic-Inorganic Materials for Photocatalytic H_2 Production

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Dogukan H. Apaydin, Dominik Eder, Alexey Cherevan

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In the year 2024, record high annual global temperatures of 1.55 °C were reported compared to pre-industrial levels resulting in several natural disasters and environmental problems. Fossil fuel consumption, one of the largest contributors towards greenhouse gas emission, must be urgently replaced with sustainable alternatives. Green H_2 possessing the highest gravimetric energy density (~120 MJ/Kg), when produced via renewable sources is an attractive solution. Unfortunately, current industrial production of H_2 via steam methane reforming produces large quantities of CO_2, further exacerbating the rising global temperatures. Photocatalytic water splitting into gaseous H_2 and O_2 using semiconductor materials that efficiently absorb solar energy provides a sustainable alternative. This direct conversion approach is not only more economical as compared to other alternatives, such as combining photovoltaics with electrolysis, but also provides a pathway to drive other important chemical reactions such as oxidative pollutant treatment or photoreduction of CO_2 into value added alcohols.

While most current photocatalysts absorb sunlight producing a large number of electron-hole pairs, often only a fraction of these participates in chemical reactions like H_2 production. This is attributed to several limiting factors such as strong excitonic binding energy resulting in high recombination rates, along with poor conductivity from low charge diffusion length. To alleviate these challenges, photocatalysts are combined with co-catalytic materials that drive the charge extraction and separation and act as active catalytic sites for the chemical reaction. Among these metal-organic-chalcogenolate-assemblies (MOCHAs) are a relative underexplored class of hybrid materials. Figure 1 shows a Ag-based MOCHA called Mithrene, denoted as AgSePh. They were first reported in 2002, but the low synthetic yield hindered their catalytic testing. Recently the development of a facile microwave assisted synthetic approach was reported producing relatively large amounts of product, allowing for testing these materials for their catalytic potential. Rabl et al. reported their first application towards electrocatalytic syngas production with a stable performance over several hours, which was the first indication towards their potential as catalysts for H_2 production.

Building on this, here, I present their photocatalytic performance towards sacrificial H_2 production under two photocatalytic reactions conditions differing in their sensitization approach, namely, quasi-homogeneous and heterogenous photosystems. In the first, we test the photocatalytic performance of different Ag-MOCHAs using visible light absorbing Ru-based photosensitizers resulting in a dynamic interaction in the solution between the two; and the latter we prepare a heterogenous composite between Ag-MOCHA and TiO_2 (using UV light) resulting in a static (heterojunction) interaction between them. We observe that in both cases AgSePh outperforms other Ag-based MOCHAs, while the performance of AgSPh and AgTePh strongly depends on the sensitization approach. In the first case, the heterogenous approach results in the formation of a AgSePh/Ag/TiO2 sandwich like structure under turnover conditions with a stable HER performance. On the other hand, the quasi-homogeneous photosystem resulted in a H2 production without any significant changes in the Ag-MOCHA, with a slight decrease overtime attributed to the degradation of the homogeneous Ru-photosensitizer. Overall, these results demonstrate the photocatalytic potential of Ag-based MOCHAs as efficient catalysts for H_2 production under various photocatalytic conditions.

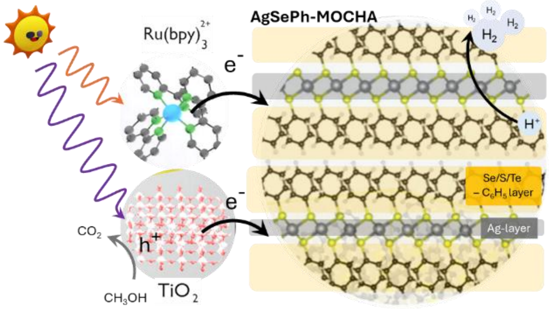

Fig. 1. AgSePh MOCHA schematic showing two sensitization approaches for photocatalytic HER

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OC-38

$CuFe_2O_4$ thin films obtained by Supersonic Cluster Beam Deposition on FTO as photocathodes for water splitting and CO_2 reduction

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$CuFe_2O_4$ has been studied during the last few years as a promising photocathode material for water splitting, nitrates and CO_2 reduction under illumination [1]. It can be usually prepared as a thin film by the sol-gel method [2], hydrothermal synthesis [3] or electrodeposition [4]. The challenge when dealing with thin films fabrication is usually related to a good stoichiometry control and optimal adhesion to the substrate. The best control over stoichiometry is usually achieved by hydrothermal synthesis, but if the oxide particle are grown directly on the FTO substrate, contained in the hydrothermal bomb, adhesion to the substrate is far from optimal. In this communication, we propose an alternative way to synthesize this material by a micro plasma (MP) Supersonic Cluster Beam Deposition (SCBD) source [5], which allows the obtainment of a $CuFe_2$ alloy in nanogranular form. The alloy is subsequently annealed in air to obtain CuO rich, ≈ 100 nm thick, $CuFe_2O_4$ thin films with optimal adhesion to the FTO substrate. These films were characterized by XRD, UV-Vis, Raman and XPS analyses. They presented good photoelectrochemical properties in 0.1 M Na_2SO_4, under visible light, and a good stability towards the hydrogen evolution reaction (HER) (Fig. 1). These films were further characterized by Intensity Modulated Photocurrent Spectroscopy (IMPS), Incident Photon Conversion Efficiency (IPCE), and tested also for CO_2 photoelectrochemical reduction, showing a promising activity.

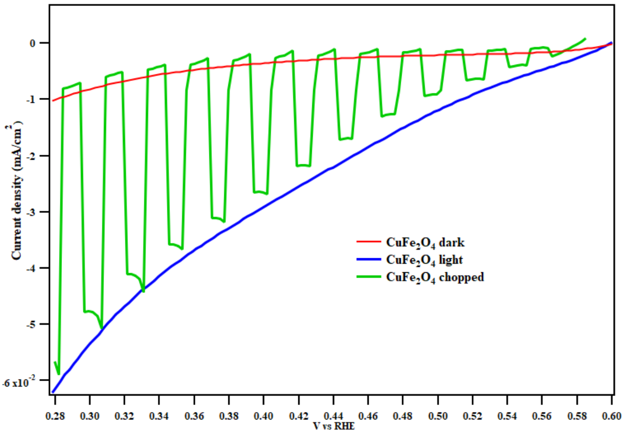

Fig. 1. LSVs in Na_2SO_4 for $CuFe_2O_4$ thin films deposited on FTO.

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OC-39

Facet-Engineered $SrTiO_3$ for Selective Photocatalytic Reduction of Nitroaromatics: Role of Morphology, Metal Co-catalysts, and Doping

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Photocatalysis has emerged as a promising alternative to traditional methods in organic synthesis, particularly for the selective reduction of nitroaromatic compounds. Conventional approaches often produce considerable amounts of waste and involve environmentally unfriendly reagents [1]. In contrast, photocatalytic systems, especially those based on TiO_2, have demonstrated nearly 100% selectivity for this reaction type [2].

In this study, we report the selective photocatalytic reduction of nitroaromatics to amines using tailored $SrTiO_3$ crystals. By systematically varying the morphology of the crystals while keeping other properties constant, we highlight the crucial role of exposed crystal facets in influencing photocatalytic efficiency and selectivity. Photoelectrochemical measurements and photodeposition studies reveal that reduction reactions primarily occur on the {001} facets, whereas oxidation processes dominate on the {110} facets. Notably, we identify an optimal ratio of these facets that enhances charge separation and significantly improves overall photocatalytic performance (Fig.1) [3].

In addition, we examine the impact of metal co-catalysts—gold, platinum, silver, and rhodium—on both charge carrier dynamics and photocatalytic activity. The influence of dopants, particularly lanthanum, on electronic properties and charge separation efficiency is also explored. The synergistic effects of facet engineering, co-catalyst deposition, and doping strategies on the reduction of nitroaromatic compounds will be presented and discussed in detail.

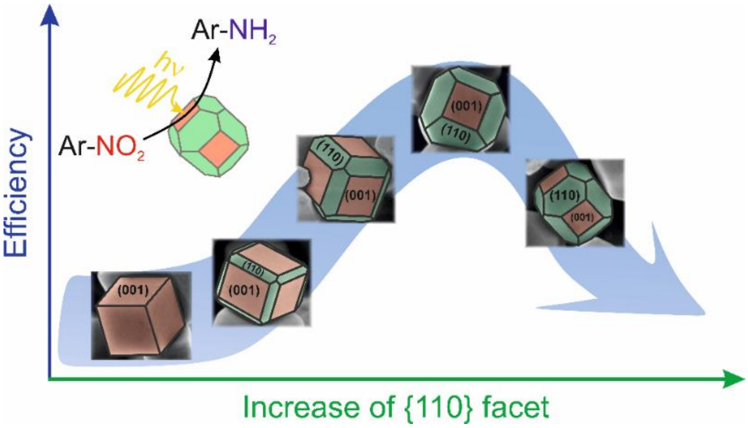

Fig. 1. Effect of tailored $SrTiO_3$ crystal on the efficiency of photocatalytic reduction of nitroaromatics.

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Acknowledgements

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OC-40

TiO_2 Photocatalysis as a Strategy to Control Free-Radical Photopolymerization

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Free-radical polymerization (FRP) is one of the most widely used techniques in photopolymerization due to its simplicity and efficiency. However, its low degree of controllability often limits its potential applications, and most studies have focused on homogeneous systems.[1] Conventional FRP setups typically rely on costly organic photoinitiators, which further restrict their practical use. In this study, we explore the integration of heterogeneous TiO_2-based systems to elucidate their mechanistic role in FRP and, ultimately, to manipulate and control specific polymerization pathways.

Our findings reveal that both intrinsic (material properties) and extrinsic (reaction conditions) factors significantly and interdependently influence polymerization behavior through direct and indirect monomer activation mechanisms (Figure 1).[2] Notably, the reaction pathways align with common photocatalytic trends governed by oxidation and reduction efficacy.[3] For instance, polymerization favors the reductive pathway when rutile-phase TiO_2 or hole scavengers are present, whereas the oxidative pathway is preferred with anatase-phase TiO_2 or electron scavengers. Additionally, the monomer structure and redox potential play crucial roles in determining the dominant reaction pathway. These insights suggest that, by carefully selecting an appropriate photocatalyst and optimizing reaction conditions, FRP can be precisely tuned toward selected pathways. Such an ability to tune polymerization toward oxidative or reductive pathways provides a strategic advantage in overcoming key limitations of homogeneous systems, such as oxygen inhibition and poor compatibility with aqueous media.[4] These findings pave the way for the development of more sustainable, cost-effective, and versatile photopolymerization strategies.

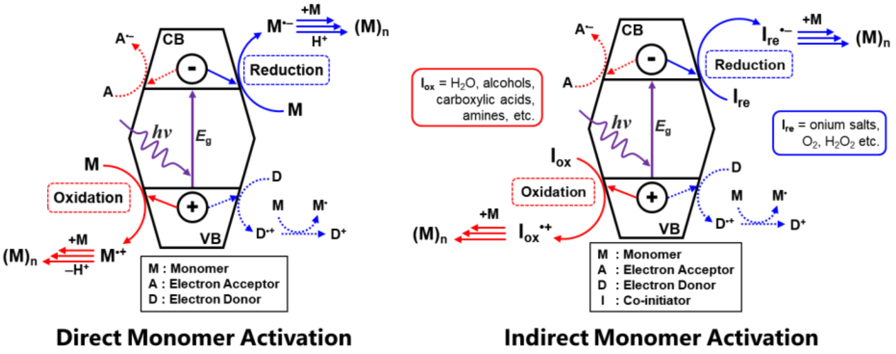

Fig. 1. Schematic representation of TiO_2-mediated free-radical photopolymerization pathways.
The oxidative pathway (red lines) and reductive pathway (blue lines) are dictated by the photocatalyst phase, reaction conditions, and monomer properties. Broken lines indicate complementary reactions that complete the redox cycles.
The terms I_{re} and I_{ox} denote the electrophilic (oxidizing agent) and nucleophilic (reducing agent) co-initiators, respectively.

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Acknowledgements

This work was supported by the National Science Centre (NCN), Poland, within the OPUS 21 Project (2021/41/B/ST5/04533) and Miniatura 8 Project (2024/08/X/ST5/00403).

OC-41

Methane Photocatalytic Conversion to Sustainable Solar Fuels Using Polyoxometalate-Based Catalysts

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Methane, abundant but inert feedstock, contributes significantly to greenhouse gases, primarily through combustion, which emits vast amounts of CO_2. Direct functionalization of methane to value-added fuels and chemicals is still one of the main challenges in modern science. Polyoxometalates (POM) are metal–oxygen cluster compounds with MO_x (x = 4, 5, 6) basic units, in which M is commonly a high-valent transition metal such as W, Mo, etc. and central atoms, which can be substituted by various heteroatoms. Polyoxometalates are a unique class of multi-electron transfer catalysts, which have attracted considerable interest due to their tuneable geometric and electronic properties, elemental composition, skeleton structure, valence state, redox properties and stability.

This work investigates POM-based photocatalysts, specifically Ag- and Pd-phosphotungstic acid/TiO_2 nanocomposites, for selective methane conversion into carbon monoxide, ethane, and acetic acid under ambient conditions. Unlike traditional photocatalysts, POMs facilitate efficient charge separation through their electron storage capacity and enable precise electronic tuning via ligand-to-metal charge transfer (LMCT). For instance, AgPW/TiO_2 catalysts demonstrated [1] exceptional performance in methane partial oxidation, achieving high carbon monoxide selectivity with a quantum efficiency of 7.1% at 362 nm. The reaction proceeds via surface methyl carbonate intermediates, stabilized by the POM's redox versatility. Similarly, a photochemical looping strategy using Ag-heteropolyacid-TiO_2 enabled [2] near-quantitative ethane formation through selective recombination of methyl radicals under illumination. Ex/in-situ characterization (XAS, EPR, IR, XPS) revealed that the Keggin structure stabilizes cationic Ag^+ species, while POM-TiO_2 p-n heterojunctions prevent electron-hole recombination, enhancing charge transfer.

Further advancing the field, our group developed [3] a Pt-POM/TiO_2 photocatalyst for selective acetic acid synthesis from CH4 and CO in aqueous media at ambient temperature: $CH_4 + CO + H_2O \rightarrow CH_3COOH + H_2$. Here, Pt single atoms anchored on ammonium phosphotungstate sub-nanoclusters achieved 90% liquid-phase selectivity, with an acetic acid concentration of 5.7 mmol/L and a turnover number of 99. The Keggin structure's electron storage and transfer capabilities, combined with tuneable POM acidity, facilitated methane adsorption and activation. Adding water boosted [4] activity by generating •OH radicals, critical for C–H bond cleavage. In methane activation, POMs enhanced C–H bond activation through concerted proton-coupled electron transfer and reactive oxygen species (ROS) generation.

Through a combination of isotopic labelling, in situ and ex situ techniques such as EPR, EXAFS, and FTIR, along with DFT molecular simulations, the elucidation of distinct mechanisms, reaction elementary steps, and active phases in the polyoxometalate photo- and thermocatalysts was achieved. These results underscore the potential of POM-based materials to balance activity, selectivity, and stability in photocatalytic systems. By integrating POMs with semiconductors [5], plasmonic nanoparticles [6], or cocatalysts, we are able to further enhance light harvesting and charge dynamics. This research paves the way for scalable, solar-driven processes of methane utilisation to meet global energy demands while mitigating environmental impacts.

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Acknowledgements

This work has received financial support from the French National Agency for Research (Projects SolarMethaCell ANR-22-CE05-0019, PulseCoMeth ANR-22-CE50-0018, PEPR LUMA Synflux-Lumicals). Y.W. is grateful to China Scholarship Council for providing him a PhD stipend.

OC-42

Metal oxides and sulfides photocatalysts for Water Splitting and CO_2 Reduction

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Photocatalytic water splitting and CO_2 reduction using water as an electron donor are promising reactions to solve resources, energy, and environment issues, and achievement of carbon neutrality. These reactions are regarded as artificial photosynthesis, because light energy is converted to storable chemical energy [1]. In the present paper, various metal oxide and sulfide photocatalysts, and semiconductor photoelectrodes for water splitting and CO_2 reduction are introduced and discussed.

(1) Photocatalytic water splitting for green H_2 production

It is a challenging topic to develop photocatalysts responding to light with long wavelength. After surveying various materials, we found that Ir or Ru-doped $SrTiO_3$ of a metal oxide material showed the activity for water splitting up to 600 nm of visible light as a single particulate photocatalyst [2]. On the other hand, $SrTiO_3$:Rh and several metal sulfides of a H_2-evolving photocatalyst, and $BiVO_4$ of an O_2-evolving photocatalyst constructed various types of Z-schematic photocatalyst systems with Fe^{3+}/Fe^{2+}, $[Co(bpy)_3]^{3+/2+}$, $[Co(phen)_3]^{3+/2+}$, poly(2,3-dihydrothieno[3,4-b][1,4]dioxane-5,7-diyl (PEDOT) of a conductive polymer, and a conductive reduced graphene oxide (RGO) as an electron mediator and even without an electron mediator [3]. Various types of Z-scheme systems for water splitting under visible light irradiation were also successfully developed by employing Rh- and Ir-doped metal oxide powdered materials with relatively narrow energy gaps (EG) to utilize wide range of visible light [4].

(2) Photocatalytic CO_2 reduction using water as an electron donor for CCU

It is important to use water as an electron donor for photocatalytic CO_2 reduction, if artificial photosynthesis accompanied with light energy conversion is considered. Ag cocatalyst-loaded $ALa_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) and tantalates photocatalysts such as Ba-doped $NaTaO_3$ with 3.79–4.1 eV of band gaps showed activities for CO_2 reduction to form CO in an aqueous medium without any sacrificial reagents [5]. CO was the main reduction product rather than H_2 even in an aqueous medium. Especially, the Ag/$NaTaO_3$:Ba photocatalyst gave ca. 90% of the selectivity for the CO formation [6]. When Rh-Ru cocatalyst was used instead of Ag, CH_4 formed with ca. 10% of the selectivity [7]. Thus, an uphill reaction of CO_2 reduction accompanied with water oxidation accompanied with O_2 evolution was achieved using the Ag- and Rh-Ru-loaded metal oxide photocatalysts.

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OC-43

Photo-promoted Thermocatalytic Methanol Steam Reforming over Plasmonic Metal Nanoparticles for Hydrogen Production

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Thermo-photo catalysis is an interesting approach to reduce the large energy consumption of thermal catalysis and address the low efficiency of photocatalysis [1]. For instance, this approach can be used to reduce the thermal input required to release hydrogen (H_2) from methanol. Hydrogen (H_2) is widely regarded as a viable energy carrier for achieving net-zero emissions; However, large-scale storage and transportation pose significant challenges. Liquid organic hydrogen carriers, such as methanol, offer a promising solution to these obstacles, but sustainable methods for releasing hydrogen from methanol are still critically needed. In this work, we investigated the thermo-photo catalytic (TPC) methanol steam reforming (MSR) over plasmonic metal nanoparticles, namely Cu and ZnCu alloy, in the presence of TiO_2 [2]. Under standard solar irradiation, the TPC hydrogen production rate over the plasmonic metal nanoparticles was higher than that of the thermocatalytic (TC) MSR process. TiO_2 was essential for enhancing the TPC efficiency (Fig. 1a) and a strong correlation between the hydrogen production rate and the metal plasmonic absorption spectrum was observed (Fig.1b).

The enhancement in the TPC activity in the presence of TiO_2 can be explained by considering the metal-semiconductor interaction. The work function of Cu typically ranges from 4.5 to 4.7 eV, which aligns well with that of TiO_2 (4.6–5.3 eV) [3]. This alignment facilitates the injection of hot electrons from the conduction band (CB) of Cu to the CB of TiO_2. Under solar light illumination, energetic hot electrons can be generated in the plasmonic Cu via intra-band (between the Fermi level and the sp conduction band) or inter-band (between the d band and sp conduction band) transition [4]. These high-energy hot electrons can be injected into the CB of TiO_2. The Schottky junction formed at the TiO_2/Cu interface could trap the transferred hot electrons and prevent their rapid recombination by delaying their transfer back to Cu. As a result, electron-rich sites can be formed at the Cu/TiO_2 interface. Simultaneously, the surface electronic state of Cu becomes positively charged due to electron depletion, leading to the formation of electron-deficient $Cu^{\delta+}$ sites. The electron-rich sites at the TiO_2/Cu facilitate the hydrogen evolution reaction, while the electron-deficient $Cu^{\delta+}$ sites promote C–H and O–H bond cleavage, ultimately yielding CO_2.

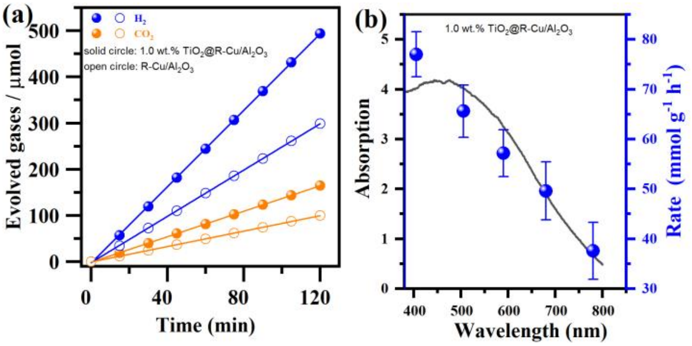

Fig. 1. (a) Time-profile of TPC H_2 and CO_2 production via MSR over plasmonic Cu supported on Al_2O_3 in the presence of TiO_2 (1.0 wt.% TiO_2@Cu/Al_2O_3) and the absence of TiO_2 (Ru-Cu/Al_2O_3) at a temperature of 200 °C and 1.0 sun illumination, and (b) action spectrum of 1.0 wt.% TiO_2@Cu/Al_2O_3 catalyst

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Acknowledgements

The authors extend their appreciation to the Deanship of Research Oversight and Coordination (DROC) at KFUPM and Saudi Aramco for funding this research work through the internal project # H2FC2306 and the external project# CHES2221.

OC-44

(Photo)thermal chemical looping dry reforming of CO2 and CH4 using Cu/Au and Ni/Au modified TiO2 photocatalysts

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The accumulation of greenhouse gases and the consequent rise in the average global temperature have become a major problem [1]. Most of these greenhouse gases are made up of carbon dioxide (CO2) and methane (CH4). It is imperative that these gases are removed to mitigate the effects of climate change. Dry reforming of methane (DRM) is an alternative to these processes to generate syngas and this approach is of particular interest as it utilizes both CO2 and CH4 as feedstock. However, the drawbacks of DRM are low selectivity and high energy input [2]. Chemical looping DRM has been shown to lower the activation energy and to allow for higher selectivity by suppressing side reactions that can occur in conventional DRM. Another side, photocatalysis is used to lower the kinetic barrier for the molecule activation and allows the conversion of abundant solar energy to chemical energy. The integration of photocatalysis with thermal chemical looping dry reforming emerges as a promising strategy. A photocatalyst such as TiO2 is both abundant and inexpensive, thus making it a suitable photocatalyst for industrial applications. However, the application of TiO2 is limited to UV light due to its large band gap. A wide range of options is discussed in the literature, which shows that noble metals are very efficient for DRM reactions. Nevertheless, due to their high price and limited availability, their utilization in large-scale industrial applications is challenging. One solution is to decorate non-noble metals with noble metals [3,4]. In this study, the photothermal chemical looping of CO2 and CH4 using Cu/Au and Ni/Au modified TiO2 photocatalysts was studied in home-made continues photoreactor system (Figure 1). For this purpose, a commercial TiO2 photocatalyst and synthesized 0.5 wt% Au-TiO2 and Cu/Au-TiO2 photocatalysts with a conc. of 0.25 – 2.00 wt.% Cu and Ni/Au-TiO2 photocatalysts with a conc. of 0.25 – 2.00 wt.% Ni. Initially, screening experiments were conducted to evaluate the performance of these photocatalysts in terms of H2 and CO production, H2 selectivity, and carbon balance. Based on the screening tests, the best performing photocatalysts was investigated further under various reaction conditions. The investigated parameters were the photocatalyst dosage, temperature and the reaction sequence. In comparison to the Au-TiO2 photocatalyst, the presence of Ni and Cu enhance the rate of production. This may be attributed to the dispersion of these metals into the lattice. The overall trend indicates that the Cu/Au-TiO2 photocatalysts exhibit a slightly higher rate of CO2 reduction and consistent H2 production rate across varying concentrations. A comparison of the synthesized photocatalysts shows that 1 wt.% Cu exhibits the highest rate of CO production. Regarding H2 production, the 1 wt.% Cu photocatalyst also exhibits a better performance than the Ni/Au-TiO2 photocatalysts, except for the 1 wt.% Ni photocatalyst.

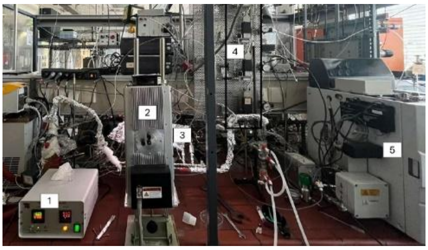

Fig. 1. Experimental setup (1- thermostat, 2- 1000 W lamp, 3- reactor, 4- mass flow controllers (MFC), 5- GC).

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This work has received financial support from the Federal Ministry of Education and Research of Germany through the"CO2-WIN initiative" under the grant number 033RC024A.

OC-45

Photoreforming of organics for H_2 production in the presence of Nb_2O_5 or TiO_2 - carbon photocatalysts

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The conversion of solar energy into other energy vectors is a promising approach to address the challenges of global sustainability. In this framework heterogeneous photocatalysis can be useful to obtain hydrogen from solutions of biomass derivatives. Photoreforming is a process that exploits the redox capacity of photocatalysts upon illumination to simultaneously obtain the reduction of H^+ to hydrogen gas and the oxidation of organic compounds. Therefore, the photocatalytic hydrogen production with simultaneous organic oxidation to obtain higher added value products or to oxidise pollutants has gained increasing attention [1,2]. In this work both bare Nb_2O_5 and TiO_2 as well as their composites with graphene (G) and graphene oxide (GO) have been prepared, physico-chemically characterized and tested as photocatalysts for the photo-reforming of aqueous solutions of ethanol, glycerol and microplastics as polyethylene terephthalate (PET) or polylactic acid (PLA) in the absence and in the presence of Pt corresponding to 1% Pt w/w relative to the total mass of catalyst.

Previous investigations evidenced good activity of Nb_2O_5 in photo-reforming, with results comparable to that obtained in the presence of TiO_2, the most used material [3]. To enhance the TiO_2 and Nb2O5 photo-reforming activity the combination of these semiconductors with carbon materials as graphene (G) or graphene oxide (GO) has been explored [4]. The strategy is addressed for the semiconductor oxide to act as photocatalyst, while G or GO would play the role of electron reservoirs, facilitating the transfer of electrons to the reaction sites by exploiting the remarkable characteristics of graphene such as the large surface area and high carrier mobility that enable it to capture and transfer photoinduced electrons.

The photo-reforming was performed both under LED-UV or natural solar irradiation. The amount of the home prepared carbon material in the composites ranged from 5% to 20% relative to the mass of the oxide semiconductor (TiO_2 or Nb_2O_5). Nb_2O_5 was synthesized through a hydrothermal process using Ammonium Niobium Oxalate as precursor whereas TiO_2 was commercial Evonik P25. The used Graphene was commercial while Graphene oxide was obtained in our laboratory by a modified Hummers method followed, in some cases, by a hydrothermal treatment. The composites were prepared by an ultrasonic treatment of a suspension in acetonitrile containing the suitable amount of graphene or graphene oxide along with the semiconductor.

Ethanol and glycerol can be easily oxidized with respect to microplastics, so yielding higher H_2 amounts. Composites based on TiO_2 were the most active, particularly in the photo-reforming of aqueous solutions of ethanol. The highest H_2 production was achieved in the presence of the composite TiO_2-graphene with mass ratio 10:1 in the presence of Pt using ethanol as the hole scavenger. In these conditions, the H_2 productivity was of 311 $mmol \cdot h^{-1} \cdot g^{-1}$ with an apparent quantum efficiency (AQE) of 100% under UV light and 13 $mmol \cdot h^{-1} \cdot g^{-1}$ with AQE 18% under natural sunlight irradiation. Further experiments in the presence of glycerol and real biomass derived solutions are under study and promising results have been obtained, for instance, the photo-reforming of the glycerol aqueous solution under natural solar light irradiation have given a H_2 productivity up to 26 $mmol \cdot h^{-1}\ g^{-1}$.

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Acknowledgements

This research was funded by the CETPartnership, under the Joint Call 2023. The CETPartnership's research projects are co-funded by the European Commission (Grant Agreement No. 101069750) and the national funding organizations listed on the CETPartnership website.

OC-46

Degradation Pathways Under Hydrothermal Catalysis Assisted by Photocatalysis for energy production

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The energy crisis currently highlights the urgency of designing innovative, sustainable and profitable processes. Faced with the depletion of traditional resources, exploring alternative energy solutions becomes essential. Photocatalysis under pressure and moderate temperature (photo-hydrothermal catalysis) is emerging as a promising approach to address the challenges of the energy. Actually, previously we found the formation of more H_2 production compared to individual processes and new products corresponding to dehydration and hydrogenation reactions [1]. In this study, our objective was to work with small organic molecules having only one or two carbons and OH, CO or COOH function alone or in pairs to better understand the chemical pathway in presence of hydrothermal catalysis assisted by photocatalysis (PTUV). In all cases gas and liquid phase were analyzed.

Except for glyoxylic acid, oxalic acid and glyoxal, under PTUV more H_2 was formed in presence of all the other molecules, methanol, ethanol, ethylene glycol, formic acid, acetic acid and glycolic acid compared to individual process, photocatalysis (PUV), and hydrothermal reaction (PT) (Figure 1).

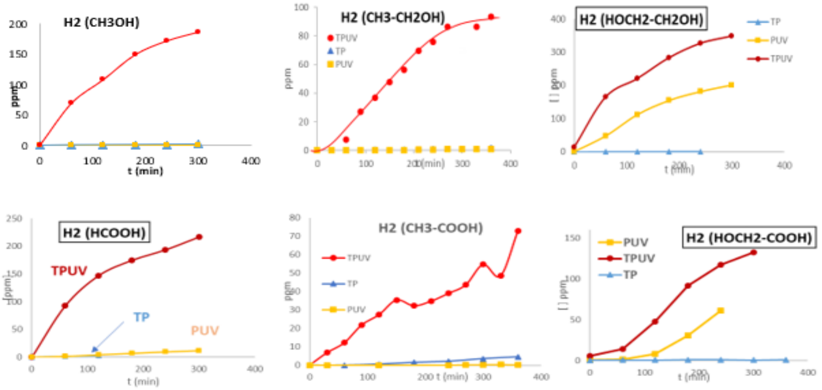

Fig. 1: H2 production as a function of time for methanol, ethanol, ethylene glycol, formic acid, acetic acid and glycolic acid in presence of TiO2 UV100 by photocatalysis UV-A (PUV), hydrothermal process (120°C, 5 bar) and photocatalysis assisted by hydrothermal process (PTUV)

Moreover, we also confirmed the formation of new product by PTUV in presence of ethanol and ethylene glycol corresponding to ethylene and acetaldehyde issue to dehydration product favoured by temperature favoured by the generation of more H^+ coming from both photocatalysis (TiO_2, UV-A) and auto-protolysis of water under P,T.

However, the degradations of these molecules are relatively low (<20% after 6h of reaction in presence of 500 ppm of initial molecule and TiO_2 UV-100) not allowing to determine the selectivity of these new compounds.

In presence of glyoxal and glyoxylic acid, hydrogenation of aldehyde function was observed generating glycolic acid in both cases and also oxalic acid in the case of glyoxylic acid. Their formations have been attributed to Cannizaro reaction issue from the generation of OH- favored in presence of temperature. Besides H2 and the different product previously mentioned, CO, CO_2, CH_4, formic acid and formaldehyde was also formed together with glycolaldehyde.

The identification of all these compounds and their quantification shows that hydrothermal catalysis assisted by photocatalysis allows to improve the charge separation and generate more H2 in presence of alcohol and acid function and formed more H^+ and OH^- favouring dehydration reaction in the case of alcohol and Cannizaro reaction in presence of aldehyde function.

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This work has received financial support from PEPR SPLEEN/ECOCHEM

OC-47

Photo-reforming of organic compounds for the simultaneous production of hydrogen and value-added chemicals

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The photo-reforming has been considered a promising technology for the future sustainable energy development, based on the capability of a photocatalyst to simultaneously drive the oxidation of organics coupled with the production of hydrogen gas, using solar energy [1]. Moreover, in parallel the cogeneration of valuable chemical products, such as ammonia (fertilizer), could be carried out, treating water matrices rich in nitrates, one the most abundant ground and surface-water contaminants, amended with reducing sacrificial agent [2].

A significant enhancement of the photo-catalytic activity has been demonstrated in the presence of several reducing sacrificial agents, such as methanol, ethanol, glycerol, glucose, in comparison with the water splitting [1].

However, the consumption of valuable and expensive hole scavengers makes this process unfeasible from an economic and environmental point of view. In this context and in alignment with the principle of circular economy, research needs to be focused on the potential application of several types of industrial wastewaters (IWWs including winery, chemical manufacturing, biodiesel production, pharmaceutical, etc), taking advantage of the high concentration of chemical compounds naturally present in their composition that can act as sacrificial agents.

Glycerol is an abundant by-product in biodiesel production and two types of water matrices amended with crude glycerol were treated at pilot plant scale (total volume 25L) under natural solar radiation and anoxic conditions. The gas-liquid system consisted of a 10 L stainless-steel tank connected to a Compound Parabolic Collector (CPC) photoreactor, inclined at 37◦, with a sun-exposed surface area of 2.1 m^2, illuminated volume of 14 L and a liquid recirculation flow rate of 20 L/min. N_2 gas was used both to purge O_2 from the system and to operate in a continuous gas flow, measuring periodically the gas stream with an on-line gas chromatograph (Agilent MicroGC 990). The reaction operating conditions (catalyst type and its concentration, water matrix, concentration of reducing sacrificial agent and the experimental time) were varied in order to evaluate their effect on the photocatalytic activity and maximize the hydrogen production rate. 100 mg/L of TiO_2:CuO (10:1) photocatalyst and 0.075 M of glycerol were found to be the optimal conditions. Subsequently, under these experimental conditions, two IWWs, diluted to achieve the optimal concentration of sacrificial agent, were previously pre-treated with coagulation-flocculation process to remove turbidity, suspended solids and soaps. H_2 production of 8-10 µmol/kJ was achieved with the two types of IWW after 180 min.

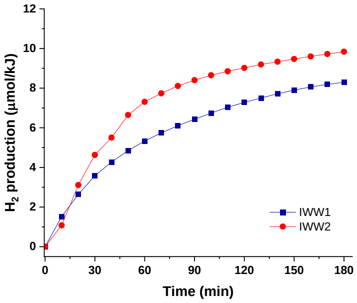

Fig. 1. Hydrogen produced during experiment with two IWWs after coagulation-flocculation pre-treatment. Reaction conditions: Catalyst: TiO2:CuO (10:1), [Glycerol]=0.075M, [Catalyst]=100 mg/L, V= 25 L, anoxic conditions.

Therefore, through an efficient photocatalytic remediation process, IWWs could be treated, converting waste into a valuable solar fuel.

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Acknowledgements
The authors would like to acknowledge to the financial support from the European Union's Horizon Europe research and innovation programme (HORIZON-CL5-2024-D3-01) under the SPECTRUM project (grant agreement No 101172891).

OC-48

Photoconversion of aqueous carbon dioxide into aliphatic acids using copper and iron oxides at solar-to-chemical conversion efficiency of ~5%

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Harnessing and utilizing sunlight at high efficiency have represented an enormous challenge to the achievement of a carbon neutral society over the past four decades. Photocatalysis uniquely mimics natural photosynthesis in terms of light absorption and conversion, as well as storage of the absorbed photon energy into chemical bond energy [1-18]. Despite this similarity, the development of low cost photocatalysts capable of selectively producing liquid chemicals from CO2 and water with efficiency and durability comparable to those in typical photosynthesis remains a great challenge. Most of the photocatalyst suspension systems produce mixtures of gas and liquid products at poor efficiencies, whereas electrically biased film systems exhibit a near-commercial gas production efficiency, albeit only for disappointingly short periods. Herein, we report the facile, environmentally benign synthesis of CuFeO2 and CuO binary films via electrodeposition, and demonstrate that these binary films produce only liquid alphatic acid anions (C1, C2, C3, C4 or C6) from aqueous CO2 at energy efficiency exceeding natural photosynthesis, while driving O2 evolution from water on a wired Pt plate under continuous irradiation of simulated sunlight over 24 h. An as-synthesized photocatalyst film with a three-dimensional, double-layer configuration further shows the continued production of C1 for over 17 days. However, the crystalline structure and elemental state of the used photocatalysts undergo gradual chemical reduction. Such a deformation can be thermally healed by recycling the weekly used samples via oxidative annealing. Thus, a single photocatalyst sample produces formate continuously for 35 days. The photocatalyst components (Cu, Fe, and O) are earth-abundant, and the photocatalyst synthesis is straightforward, facile, environmentally benign, reproducible, and scalable. On achieving higher efficiencies in the future, the practical applicability of these photocatalysts will become enormous.

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Acknowledgements

This work has received financial support from the National Research Foundation of Korea (RS-2023-00254645 and RS-2018-NR031057).

OC-49

Dual Photocatalytic Routes for Plastic Waste Upcycling and Mineralization Using Alkalized Carbon Nitride

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The persistent accumulation of plastic waste has intensified the need for sustainable and efficient management strategies. In this study, we develop a dual photocatalytic approach utilizing alkalinized carbon nitride (Alk-CN) to simultaneously achieve the valorization and mineralization of plastic waste [1]. Under alkaline conditions, Alk-CN effectively photoreforms polyethylene terephthalate (PET) by selectively oxidizing ethylene glycol, leading to the efficient generation of hydrogen peroxide (H_2O_2) and the concurrent recovery of high-purity terephthalic acid. The catalyst also demonstrates broad substrate adaptability by enabling the photoreforming of other polyester-based plastics, such as polybutylene terephthalate and polylactic acid.

Beyond upcycling, Alk-CN facilitates the complete mineralization of trace organic residues through an advanced oxidation process, where in-situ generated H_2O_2 is photoactivated to produce hydroxyl radicals, achieving near-complete degradation of plastic-derived contaminants. Structural and mechanistic analyses reveal that the alkalization treatment enhances the photocatalytic properties of carbon nitride by improving charge separation, accelerating two-electron oxygen reduction, and suppressing charge recombination. As a result, Alk-CN exhibits high selectivity toward H_2O_2 production, stable photoreforming activity, and long-term durability across multiple reaction cycles without significant deactivation.

This work demonstrates a sustainable and effective dual-function photocatalytic strategy for managing plastic waste, offering a practical route for converting waste plastics into valuable chemicals while ensuring complete environmental remediation.

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OC-50

Controlled Periodic Illumination for Increasing the HER Efficiency Over Metal-TiO_2 Nanoparticles

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The effectiveness of catalysts and photocatalysts in accelerating multistep chemical processes is often limited when the rate-determining step matches the rate of other elementary reactions. Several strategies have been explored to enhance catalytic efficiency, among which controlled periodic illumination (CPI) is receiving increasing attention for its potential to optimize the charge transfer mechanisms under irradiation. However, its its real advantage is still debated.[1] Efficient solar water splitting is hindered by substantial overpotentials in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Even with noble metal catalysts, such as Pt, Pd, and Rh, the HER can be constrained by strong M−H bonding, which inhibits hydrogen desorption. The hydrogen absorption process is governed by the potential at the metal nanoparticle surface.[2]

In our studies, we employed CPI to overcome the limitations imposed by scaling relations and optimize the utilization of charge carriers. We hypothesized that rapid fluctuations in the photopotential were able to modulate the M-H bond at the surface of the catalyst, leading to an increase of more than 50% in HER efficiency at frequencies above 80 Hz.[3] We then demonstrated the effectiveness of CPI in enhancing photoactivity exclusively on metals with a low Tafel slope (Pt, Rh, Pd). As already underlined, the key factor is the M−H interaction, which depends on the dominant HER mechanism (Volmer-Heyrovsky or Volmer-Tafel).[4] Additionally, by modulating the duty cycle and frequency of illumination, we observed that both factors play a crucial role in enhancing the HER.[5] Using various photoelectrochemical characterization techniques, we found that CPI led to an increase in charge carrier density for all tested materials. However, only certain materials are able to exploit this excess of carriers. In fact, an increase in quantum yield was only evident in metals that are limited by H_2 desorption due to strong M−H bonds. CPI appears to reduce the energy of the M−H bond, thereby favouring hydrogen desorption. Moreover, these metals operate under a Volmer-Tafel mechanism, which allows them to function effectively during both light and dark periods.[4-5] This demonstrates the potential of CPI as an effective tool for enhancing catalytic efficiency, especially for materials constrained by the M−H bond strength.

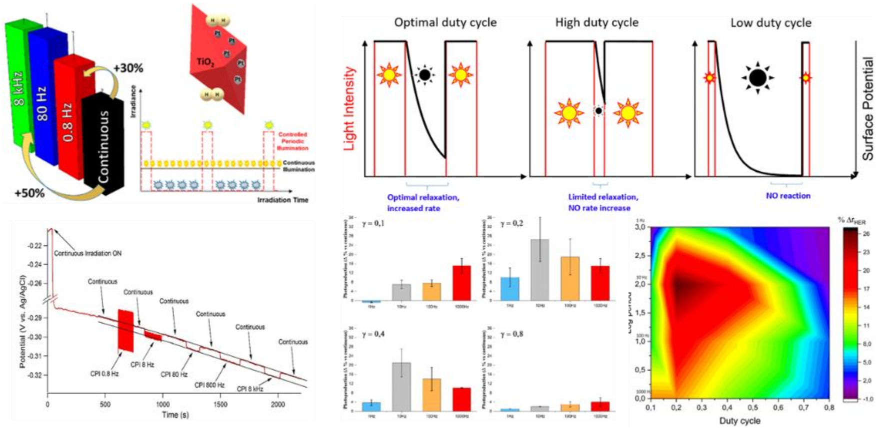

Fig. 1. Photocatalytic increase of the efficiency using CPI in the HER.

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OC-51

A Comprehensive Analytical Model for Front and Back Illuminated Electrodes in Photoelectrochemical Cells

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The deployment of carbon-free energy technologies that could compete with the price of fossil fuels is expected to be a key factor for sustaining the future energy requirements of the world population. Hydrogen is a promising energy vector that can be produced using solar energy. In this regard, tandem photoelectrochemical cells have attracted major attention as devices for green hydrogen (and other fuels) generation in the last years.[1,2] They are composed of two semiconductor-based electrodes (photoanode and photocathode) illuminated from different sides, which should exhibit complementary characteristics to work under bias-free conditions. In this contribution, we present a model for the theoretical prediction of the current-voltage characteristic curves in semiconductor-electrolyte junctions. The theory for charge carrier dynamics in the semiconductor film under light excitation is considered for building up the model equations using as input geometric and physic parameters of the electrode. Recombination in the diffusion-driven region and space-charge region are included. The analysis of limiting cases leads to simplified cases that allow the prediction of the physical properties of the semiconductor under simple experimental analysis in practical photoelectrodes. The model can be integrated into a broader analysis to predict the limits of solar-to-hydrogen efficiencies in photoelectrochemical cells for hydrogen production.

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MIDG acknowledges the financial support from Generalitat Valenciana (CIDEIG/2023/1). Authors gratefully acknowledge funding from the European Union's Horizon 2020 research and innovation programme under grant agreement no. 760930 (FotoH2 project).

OC-52

Enhanced Photocatalytic Methanol Formation through Dual Z-scheme Charge Transfer in Titania Nanotubes Co-deposited with Copper and Vanadium Oxide

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The accelerating release of greenhouse gases, particularly CO_2, has significantly contributed to global warming, posing serious environmental and societal challenges [1]. A promising strategy for mitigating CO_2 emissions is its photocatalytic conversion into methanol using titanium dioxide (TiO_2) with water as a co-reactant [2]. However, the efficiency of TiO_2-based materials is limited by their poor visible light absorption and rapid recombination of photogenerated charges [3].This study aims to enhance the photocatalytic conversion of CO_2 to methanol under simulated solar light by co-depositing copper oxide and vanadium oxide (Cu_xO, V_xO_y) onto titania nanotubes (TNTs). The co-deposited photocatalysts were synthesized using electrochemical, wet chemical, and atomic layer deposition methods and thoroughly characterized through various analytical techniques. Their performance in converting CO_2 and water vapor to methanol was then evaluated and correlated to their method of preparation.

The results (figure 1 left) demonstrate enhanced photocatalytic activity of the Cu_xO, V_xO_y-TNT catalyst, likely due to several factors: improved methanol selectivity from Cu_xO, increased surface area of TNTs facilitating CO_2 adsorption, and reduced electron-hole recombination, potentially resulting from dual Z-scheme charge transfer. To further investigate these effects, we specifically examined the dual Z-scheme charge transfer (figure 1 right) by analyzing the individual metal oxides, determining the conduction band (CB) through Mott-Schottky measurements and the band gap (BG) using UV-Vis spectroscopy. These findings highlight that co-depositing metal oxides on nanostructured photocatalysts can significantly improve their surface structure and photocatalytic properties, representing a crucial step toward more sustainable CO_2 conversion technologies.

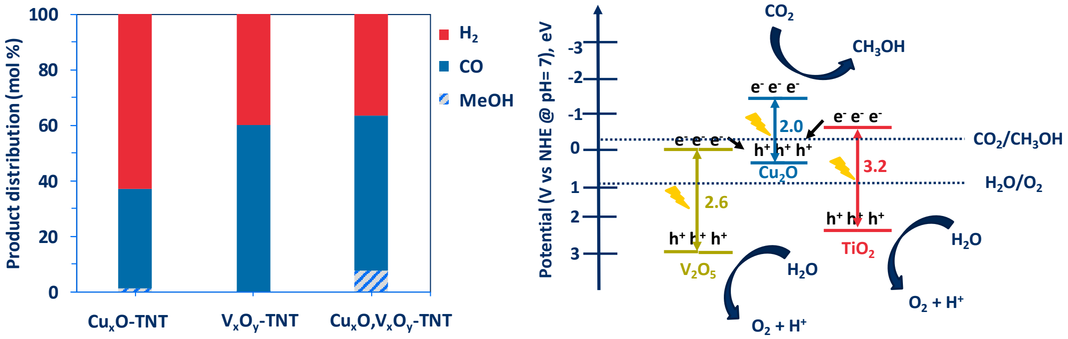

Fig. 1. (Left) Product distribution in mol% after 5 h of solar light irradiation during photocatalytic CO_2 conversion. (Right) Schematic diagram of charge transfer in the dual Z-scheme heterojunction between Cu_xO, V_xO_y, and TNT.

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This work has received financial support from the VLAIO Moonshot SYNCAT project (HBC.2020.2614), part of the Flanders Industry Innovation Moonshot initiative. P. Cool acknowledges funding from the Interreg FOTON project. The authors thank Saskia Defossé and Wouter Van Hoey from the LADCA research group at the University of Antwerp for their assistance with SEM and XRD measurements.

OC-53

Hydrogenated TiO2 nanoparticles: origin of the enhanced photocatalytic properties for the degradation of some pollutants and hydrogen production

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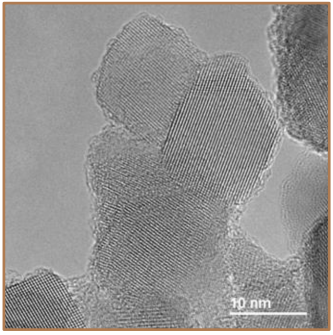
Titanium oxide continues to be one of the most studied solids today owing to its potential photocatalytic applications, in a wide variety of fields including the degradation of organic compounds in solution or the production of green hydrogen from water. In order to improve its performance, doping has been used, among other approaches, in both the cationic and anionic positions. The formation of partially reduced titanium oxide, which has been called self-doping, due to the presence of Ti3+ and oxygen vacancies, has attracted much attention in recent years as a simple way to improve the performance of this oxide [1-3].

In this contribution, a titanium oxide P25 reduced with NaBH4 is synthesized, characterized by means of transmission electron microscopy and temperature-programmed experiments in order to study its chemical properties. The NaBH4 reduction has led to the synthesis of a family of hydrogenated titanium oxide samples. Various degrees of reduction have been tested combining different heat treatments and reducing agent concentrations, giving place to a set of samples from the so-called blue-titania (mild reduction conditions, see Figure 1) to a heavily reduced black-titania.

First of all, the photodegradation of several organic dyes and chlorophenol organic molecule has been assessed, allowing to stablish a neat correlation between the degradation capacity and the pz0 value, which has been demonstrated to be directly influenced by the reducing treatment applied. Secondly, the samples have been tested in the photocatalytic water splitting reaction, under solar simulator light source in order to produce green hydrogen. Among the titania-based samples, blue-titania has shown the highest performance with a remarkable hydrogen production, overcoming the activity of TiO2-P25 reference in one order of magnitude.

The characterization of the samples through advanced Scanning Transmission Electron Microscopy techniques, using HAADF, iDPC and EELS techniques, shows the presence of surface oxygen vacancies, as well as the insertion of hydrogen in the titanium oxide structure. The work establishes a relationship between the presence of this hydrogen, the reduction of titania and its photocatalytic behavior.



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OC-54

Photoelectrosynthetic reactions on n-type semiconductor photoelectrodes

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Currently, many photoelectrochemical studies try to use n-type semiconductors for light-assisted water electrolysis and only a small amount of research has been devoted to other oxidation processes. An exception is the photoelectrochemical oxidation of organic impurities in water but these processes, as very low concentrations of impurities are targeted, are necessarily associated with low Faradaic efficiencies. In contrast, photoelectrosynthetic reactions leading to compounds of the value, such as fuels, powerful oxidants or fine chemicals would use high concentrations of starting compounds which can lead to high Faradaic efficiencies. Interesting photoelectrochemical reactions involve as starting compounds inorganic anions like I^-, Br^-, and Cl^-. These processes are interesting because they not only offer information about the amount of a generated halogen (I_2, Br_2, and Cl_2) but also a unique insight into the competitive kinetics between the oxidation of water and the selected halide. Another example is photoelectrochemical oxidation of sulphate (SO_4^{2-}) to persulphate ($S_2O_8^{2-}$), first reported by Desilvestro and Grätzel [1].

Due to their valence band position, when exposed to light, titanium dioxide (TiO_2) and WO_3 generate highly oxidizing species – valence band holes and hydroxyl radicals (OH·). For this reason, TiO_2 with a band gap energy of 3.2 eV is a widely studied semiconductor. WO_3 has the advantage of using a slightly larger part of the solar spectrum (E_g = 2.7 eV). Examples of n-type oxides usable in the visible light region are hematite (α-Fe_2O_3) and pseudobrookite (Fe_2TiO_5). α-Fe_2O_3 is a non-toxic and abundant semiconductor with the ability to absorb a significant part of the solar spectrum (E_g = 2.1 eV) [2]. Fe_2TiO_5 is a medium-wide bandgap (E_g = 2.1 eV) [3] n-type semiconductor. Fe_2TiO_5 and α-Fe_2O_3 have valence band holes with a lower oxidation potential compared to TiO_2 and WO_3. The primary objective of this study was to investigate the Faradaic efficiencies of selected photoelectrochemical oxidation reactions involving valence band processes on some oxide semiconductors, e. g. TiO_2, WO_3, Fe_2TiO_5 and α-Fe_2O_3. The first case study was the photoelectrochemical oxidation of Br^-[4]. Fig. 1 a) shows that all four semiconductors have valence bands potentials which are positive enough to enable oxidation of Br^- to the Br· radical in a direct electron transfer process. As shown in Fig. 1 b), for bromide oxidation on the four investigated semiconductors, α-Fe_2O_3, Fe_2TiO_5, TiO_2, and WO_3, a steady increase of Faradaic efficiency with solute concentration was observed, approaching a plateau with an efficiency of 100 %.

The second study was devoted to the photoelectrochemical generation of powerful oxidant ($S_2O_8^{2-}$) on TiO_2, WO_3 and $CuWO_4$. The objective of both studies is to understand how differences in the efficiencies of the tested semiconductors can be attributed to their valence band positions and the redox properties of the solute.

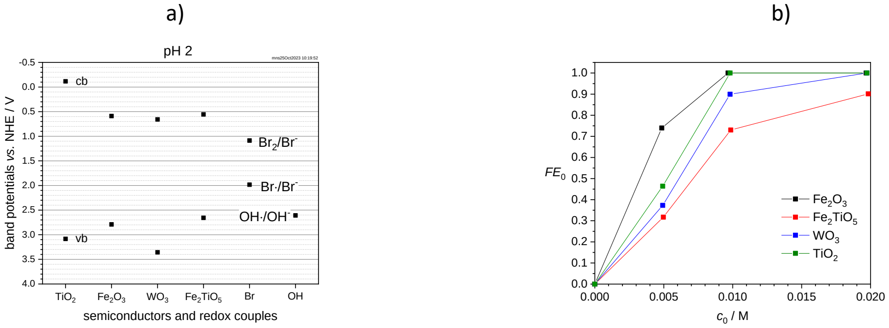

Fig. 1 a) Valence and conduction bands (vb, cb) position at pH 2 for studied semiconductors: TiO_2, α-Fe_2O_3, WO_3 and Fe_2TiO_5 and the standard redox potential of bromine / bromide and redox potentials for radicals: bromine and OH, b) comparison of the studied semiconductors for bromine generation in terms of the dependence of initial Faradaic efficiency (FE_0) on initial bromide concentration (c_0).

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Acknowledgements

This work was supported by the Czech Science Foundation (project number 23-05266S).

OC-55

Light-driven nitrogen fixation to ammonia over aqueous-dispersed Mo-doped TiO_2 colloidal nanocrystals

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Photocatalytic nitrogen fixation to ammonia holds great promise as a sustainable route powered by solar energy and fed with renewable energy resources (N_2, H_2O) [1]. This technology is currently under deep investigation to overcome the limited efficiency of the process. The rational design of efficient and robust photocatalysts is crucial to boost the photocatalytic performance. Widely used bulk materials generally suffer from charge recombination due to poor interfacial charge transfer and difficult surface diffusion [1,2]. To overcome this limitation, this work explores the use of aqueous-dispersed colloidal semiconductor nanocrystals (NCs) [3,4] with precise morphological control, better carrier mobility and stronger redox ability. Here, TiO_2 framework has been modified via aliovalent molybdenum doping, and resulting Mo-TiO_2 NCs (average size of 5 nm) have been functionalised with charged terminating hydroxyl groups (OH^-) for the production of ammonium (NH_4^+) via photocatalytic nitrogen reduction reaction (NRR) in water (Fig. 1).

Our results demonstrate both, the positive effect of Mo-doping and nanostructuration on the overall N_2 fixation performance. Ammonia production rates are found to be dependent on the Mo-doping loading. 5Mo-TiO_2 (*i.e.* 5% mol Mo) delivers the highest NH_4^+ yield rate (*ca*. 105.3 $\mu mol\ g^{-1}\ L^{-1}\ h^{-1}$) with an outstanding 90% selectivity, which is almost 4-times higher than that obtained over bare TiO_2. To understand the positive effect of Mo-doping on the NRR performance of NCs, we have developed a thorough investigation combining structural, photoelectrochemical and photophysical characterisation. Results obtained herein indicate that the substitutional doping of TiO_2 (Ti^{4+}) with higher valence molybdenum cations (Mo^{6+}) facilitates NRR by (i) providing actives sites for N_2 chemisorption; (ii) polarising N atoms p; (iii) extending light absorption, and (iv) improving charge transfer. This work expands the use of this environmental-friendly aqueous NCs processing to the development of Mo-based photocatalysts for an emerging energy application. Our findings open the door to new materials to progress on the development of NRR technologies for sustainable ammonia production.

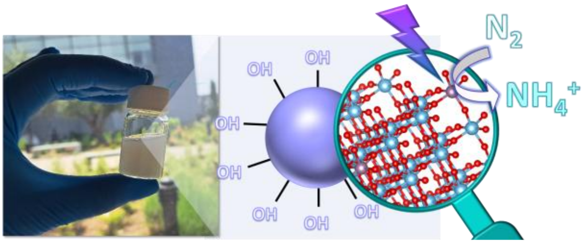

Fig. 1. Aqueous-dispersed colloidal Mo-doped TiO_2 nanocrystals.

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Acknowledgements

This work has received financial support from ARMONIA (PID2020-119125RJ-I00), NovaCO2 (PID2020- 118593RB-C22), 2D-Photo2Change (TED2021-129999A- C33), and Nhympha (PID2019-106315RB-I00) funded by MCIN/AEI/10.13039/501100011033. Additional funding has been received from the projects SOL-Future (PLEC2021- 0079069) and SolarCPP-Bat (CNS2022-135380), funded by both MCIN/AEI/10.13039/501100011033 and NextGener- ationEU/PRTR. This work received also support from “La Caixa” foundation fellowship (ID 100010434, fellowship code LCF/BQ/PR23/11980046). XAS experiments were performed at the CLAESS beamline of the ALBA synchrotron (proposal no. AV-2020074403). M.B. thanks Juan de la Cierva Incorporación grant (IJC2019-042430- I) funded by MCIN/AEI/10.13039/501100011033. G.G. acknowledges FJC2020-044866-I grant funded by MCIN/ AEI/10.13039/501100011033 and by the “European Union NextGenerationEU/PRTR”.

OC-56

Bi-based perovskite for efficient photoreduction of CO_2 to CO

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Inorganic Bi - based halide perovskites have attracted great attention in the field of CO2 photoreduction due to their excellent photoelectric conversion performance and low toxicity However, the intrinsic deep defects are still one of the main factors limiting the carrier lifetime and transmission. Therefore, CBSB-x NCs were synthesized using sonication - assisted method for controllable regulation of deep defects, and their CO2 photoreduction performances were also evaluated in this study. Among the alternatives, CBSB-1 NCs demonstrate superior catalytic performance for CO and CH4 production, exhibiting yields of 38.77 µmol·g-1 and 1.39 µmol·g-1, respectively. The physicochemical properties and corresponding mechanism of the catalyst were investigated by band structure and photoelectric characterization. The in-situ DRIFTS and DFT calculation reveal that Sb3+ facilitates the enhancement of charge transfer rate at the Bi -Br - Sb interface and expedites the swift evolution process of b-CO32- to HCOO- in the primitive chemical environment. This study establishes an empirical and theoretical basis for the application of alloyed perovskites in CO2 photocatalysis and provides novel avenues for future research.

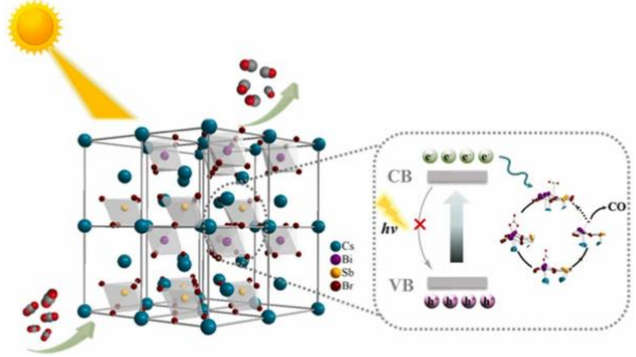

Fig. 1. Reaction mechanism of Bi-based perovskite for CO2 photoreduction.

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OC-57

Exfoliation of D-A polymers for enhancing their photocatalytic production of H_2O_2

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Hydrogen peroxide (H_2O_2) is a key oxidant in green chemistry, but its conventional anthraquinone-based production is energy-intensive and environmentally harmful. H_2O_2 generation by solar-assisted photocatalysis offers a sustainable alternative [1]. However, this process requires photocatalysts with efficient charge separation and band alignment to favor the $2e^-$ oxygen reduction reaction (ORR) while minimizing $1e^-$ pathways. Donor-Acceptor (D-A) conjugated polymers are promising candidates due to their π-conjugation, which enhances charge transfer and ORR selectivity. However, their low surface area limits the interaction between the reaction medium and the catalyst, constraining their efficiency [2]. This work explores different exfoliation methods to improve the surface area and photocatalytic performance of Furan(D)-Pyrrole(A) polymers (FPP) (structure shown in Fig. 1a) for H_2O_2 production. Pristine FPP was obtained via low-temperature polycondensation of a urea-glucose mixture at 200°C and exfoliation using thermal (T_{exf}: 150, 200, 250°C in air; 250°C in N_2), chemical (45% H_2SO_4, 35% HCl, 50% HNO_3), and mechanical (planetary ball milling at 400, 600, 800 rpm) methods. The exfoliated samples were characterized by XRD, UV-Vis DR, XPS, PL, FTIR, N_2 adsorption-desorption, Mott-Schottky, EIS, and photocurrent tests. Photocatalytic activity was evaluated in O_2-saturated water under a 500 W Xe lamp (PXE-500), and H_2O_2 was quantified by colorimetry. As shown in Fig. 1b, pristine FPP exhibited a high photocatalytic activity (1382 $\mu M\ H_2O_2\ g^{-1}\ h^{-1}$) despite its low surface area (3 $m^2\ g^{-1}$), highlighting the efficiency of its charge separation and band alignment. Thermal exfoliation at 200°C improved the surface area (7 $m^2\ g^{-1}$) and H_2O_2 production, peaking at 1573 $\mu M\ g^{-1}\ h^{-1}$. By increasing T_{exf} to 250°C, however, structural rearrangements disrupted the π-conjugated network impairing charge transport and photocatalytic efficiency. Chemical exfoliation of FPP with H_2SO_4 and HNO_3 caused oxidative defects that degraded the polymer structure [3] reducing the performance for H_2O_2 production. In contrast, HCl preserved chemical stability and increased the surface area to 8 $m^2\ g^{-1}$, achieving 1663 $\mu M\ H_2O_2\ g^{-1}\ h^{-1}$. Mechanical exfoliation proved to be the most effective strategy, enhancing the photocatalytic activity without degrading the polymer backbone. Shear forces fragmented the material while maintaining π-conjugation. At 800 rpm, the highest H_2O_2 production (1734 $\mu M\ g^{-1}\ h^{-1}$) was achieved with an increase of surface area to 11 $m^2\ g^{-1}$. XRD, FTIR, and XPS confirmed significant structural modifications at high temperatures and by H_2SO_4 and HNO_3 use, correlating with the decreased performance. UV-Vis spectra showed a broad absorption in the 400–800 nm range, with greater variations in mechanically and chemically exfoliated samples. In particular, band gap reductions below 1.1 eV were observed, which likely hindered efficient charge separation, explaining the lower photocatalytic performance in cases such as T-250 and C-H_2SO_4. EIS revealed notable variations in charge transfer. Lower-performing samples exhibited a higher resistance, linking the structural degradation to reduced efficiency. As shown in Fig. 1c, mechanical exfoliation progressively lowered the charge transfer resistance with increasing rpm, while C-HCl and T-200 displayed the lowest values, reinforcing their superior charge transport properties.

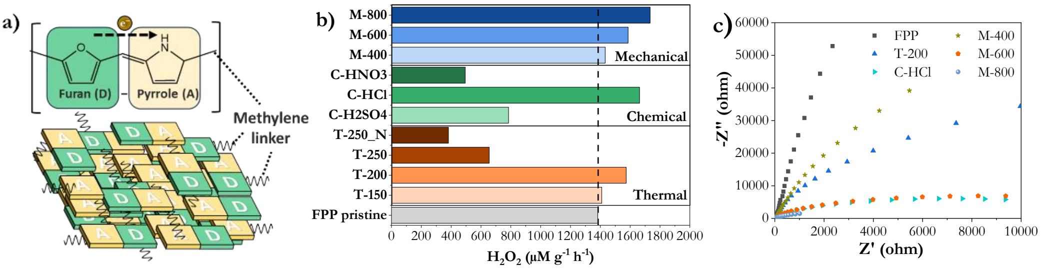

Fig. 1. a) FPP structure, b) H_2O_2 production of synthesised materials, and c) EIS plots of selected photocatalysts.

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Acknowledgements

The authors acknowledge the financial support to European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement № 101007578, SusWater project; and Agencia Estatal de Investigación (AEI) and Ministerio de Ciencia e Innovación (AquaEnAgri project, PID2021-126400OB-C32).

Understanding and Enhancing the Photocatalytic NOR on *d-Metal-modified TiO₂*

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The catalytic fixation of atmospheric dinitrogen plays a pivotal role in providing humankind with sufficient sustenance. Herein, the HABER-BOSCH and OSTWALD processes remain to this day the key thermocatalytic approaches to provide nitrate-based fertilizers, among other products [1]. With the ammonia oxidation in the OSTWALD process being highly exothermic (- 907 kJ mol^{-1}) [2], however, lies the fundamental thermodynamic issue of ammonia's main energy content being lost. A more direct approach is thus desirable yet proves difficult due to the high activation barrier of breaking the dinitrogen triple bond. Photocatalytic fixation of dinitrogen is laid out in two different pathways: The reductive route with ammonia being the target product, or alternatively, the oxidative valorisation leading to nitrate formation.

Titanium dioxide has already been shown to display noticeable, if rather low catalytic activity towards photodriven NOR [3]. Previous works have furthermore delivered proof that active sites in thermocatalytic methanol and isopropanol oxidation were also active towards a light-induced pathway of the same reaction [4,5]. Thus, titania was modified to include co-catalytic metals known to facilitate the activation of nitrogen, such as Fe and Mo, and V for oxygen activation. Additionally, as a fundamental concept of catalysis, both the forward and the reverse reaction are facilitated. Hence, the NOR-activity of titania-supported active sites for DeNOx catalysis based on Pd was investigated as well. Herein, we found a considerable improvement the photocatalytic performance.

To identify kinetic bottlenecks, ongoing *in-situ* vibrational spectroscopic and activity studies aim to provide a better understanding of the role of deposited active sites on titania, and to identify possible interfering and/or structural effects by native surface carbonates to improve the catalytic potential of TiO2 in the photodriven NOR.

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Acknowledgements

This work was funded by the German Research Foundation (DFG), as part of the priority programme SPP 2370 "Nitroconversion".

OC-59

$BiVO_4$ - Liquid Junction Photovoltaic Cell with 0.2% Solar Energy Conversion Efficiency

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$BiVO_4$ is an important photoanode material for water oxidation, but its photoelectrochemistry regarding the triiodide/iodide redox couple is not well understood. Here, we use a combination of open circuit potential measurements, photoelectrochemical scans, and liquid surface photovoltage spectroscopy (SPS) to confirm that $BiVO_4$/triiodide/iodide electrolyte contacts produce up to 0.55 V photovoltage under 23 mW/cm^{-2} illumination from a 470 nm LED. Inspired by these results, we construct In/FTO/$BiVO_4$/KI(I_2)aq/Pt sandwich photoelectrochemical cells from electrochemically grown 0.5 x 0.5 cm^2 $BiVO_4$ and Mo-doped $BiVO_4$ films. Under AM 1.5 illumination, the devices have up to 0.22 % energy conversion efficiency, 0.32 V photovoltage, and 1.8 mA cm^{-2} photocurrent. Based on SPS, hole transfer to iodide is sufficiently fast to prevent the competing water oxidation reaction. Mo-doping increases the IPCE to up to 55% (at 425 nm under front illumination) by improving the BiVO4 conductivity, but this comes at the expense of a lower photovoltage resulting from recombination at the Mo defects, and a detrimental Schottky junction at the interface with FTO. Additional photovoltage losses are caused by the offset between the $BiVO_4$ valence band edge and the triiodide/iodide electrochemical potential, and by electron back transfer to iodide at the FTO back contact (shunting). Overall, this work provides the first example of a $BiVO_4$-liquid photovoltaic cell and an analysis of its limitations. Even though the larger band gaps of metal oxides constrain their solar energy conversion efficiency, their transparency to visible light and deep valence bands make them suitable for tandem photovoltaic devices.

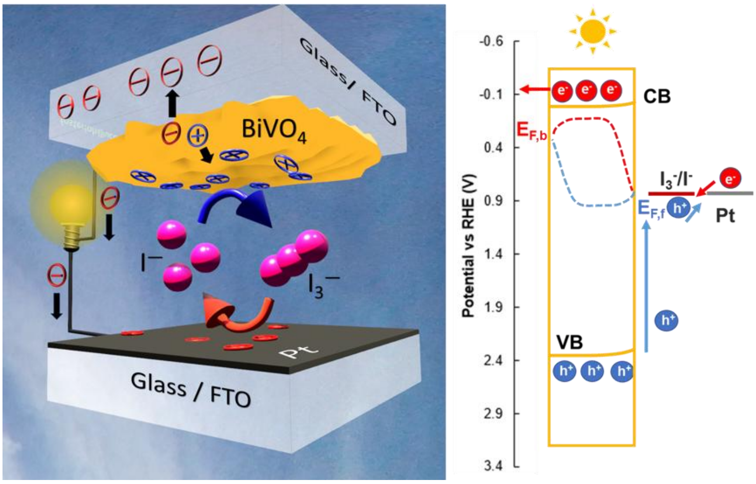

Fig. 1. Band bending in a) p-GaP and b) n-type GaP photocatalyst at the semiconductor-cocatalyst (M) and semiconductor-liquid interfaces and corresponding charge separation under illumination.

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OC-60

Transparent ZnO electrodes with near metallic conductivity from solution-based methods: how precursor design is key to scalable technology

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Transparent conducting oxides (TCOs) are metal oxides with unique optoelectronic properties for energy production applications - they are transparent to the visible range of the spectra while exhibiting electrical conductivity. ITO or FTO contacts fabricated by physical deposition methods find extensive use as transparent electrodes at research level in a variety of applications, as they exhibit near-metallic resistivity (10^{-4} - 10^{-5} Ω·cm) and avoid shadowing over a subsequent active layer. However, the low scalability of these methods alongside the scarcity of Indium and the negative environmental impact of fluorinated scrubbers have long impeded the implantation of transparent electrodes in large-scale manufacturing of optoelectronic devices. [1]

ZnO is earth abundant and environmentally friendly, with high potential as alternative upon extrinsic doping. Nevertheless, there is a limitation on available precursors for scalable solution-based synthesis of ZnO, as carbon-free precursors are highly pyrophoric (*i.e.* $ZnEt_2$) and ambient stable precursors have high carbon content (*i.e.* $Zn(acac)_2$). Research on n-type doped (Ga, Al) ZnO electrodes over the last decade has mostly reported TCO coatings with either fair electronic properties (10^{-3} Ω·cm) through a non-scalable process or poor electronic properties (10^{0} - 10^{-1} Ω·cm) through a safe and scalable process. [2] Ultimately, it is the chemical environment of Zn atoms in the precursor source that determines the nucleation and growth regimes,[3] for which Zn centres with unsaturated coordination and volatile ligands with low-carbon content are key to develop molecular precursors with tailored decomposition.

This work reports the design of a molecular precursor with a pre-organised structure designed under these principles, which decomposes cleanly (Fig. 1a) to form highly compact and crystalline ZnO coatings (Fig 1b-c) *via* aerosol-assisted chemical vapor deposition (AACVD). The synthesis of these TCO coatings is compatible with the use of commercial doping reagents ($Ga(acac)_2$) resulting in the fabrication of highly self-textured transparent electrodes with near-metallic resistivity (10^{-4} Ω·cm) (Fig. 1d).[4] These results represent a significant advance for the preparation of devices for solar to electricity conversion, with relevance as crystallographic template and as layer in photoactive heterojunctions.

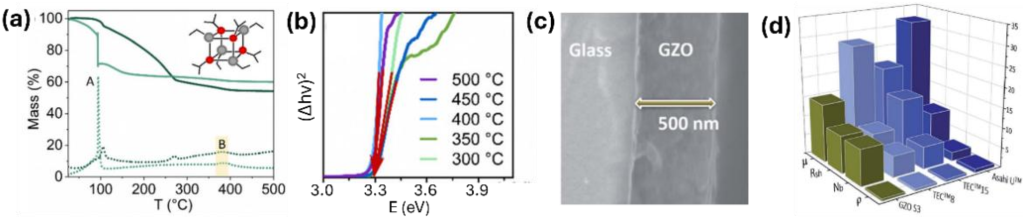

Fig. 1. (a) Thermogravimetric (full lines) and differential scanning calorimetry (broken lines) of ethylzinc isopropoxide precursor in inert (dark) and oxidized (light) atmosphere, showing a clean decomposition in air. (b) Bandgap calculation from transmittance data of ZnO thin films prepared *via* AACVD using Tauc-plot for direct bandgap metal oxide semiconductors showing high crystallinity at temperatures as low as 300 °C. (c) Cross sectional SEM image of Gallium-doped ZnO (d) Electronic properties of Gallium-doped ZnO compared to industrial standards TEC8, TEC15 and AsahiU.

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Authors acknowledge the financial support of the Spanish Ministry of Science and Innovation and the Spanish State Research Agency (MCIN/AEI/10.13039/501100011033) through the project POLLUTWIN (TED2021-129162B-C21) and the European Union (NextGenerationEU/PRTR). C. S.-V. would like to thank the Regional Government of Madrid for financial support through Programa de Atracción de Talento "César Nombela" 2023 (2023-T1/ECO-29048).

OC-61

Unraveling the Nature of Hole Polarons as OER Intermediates in Titanium Oxides via Ultrafast Optical Spectroscopy

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Despite decades of research, the mechanistic details of photocatalytic water splitting on TiO_2-based materials remain incompletely understood. Growing evidence points to hole polarons as key intermediates in enabling the oxygen evolution reaction (OER), yet the precise identification remains challenging.

Recent work has enabled the assignment of excited-state absorption spectra to distinct hole polaron configurations. Different intermediates dominate the picosecond regime depending on the titanium oxide material: terminal $O^{\bullet-}$ in TiO_2 and lateral $Ti_2O^{\bullet-}$ in $SrTiO_3$.[1] The shifted absorption maxima observed experimentally could be rationalized using DFT and TD-DFT calculations, which identify distinct origins of the optical transitions as the primary cause (Fig. 1). However, the broad spectral width and behavior under different reaction conditions require further investigation.

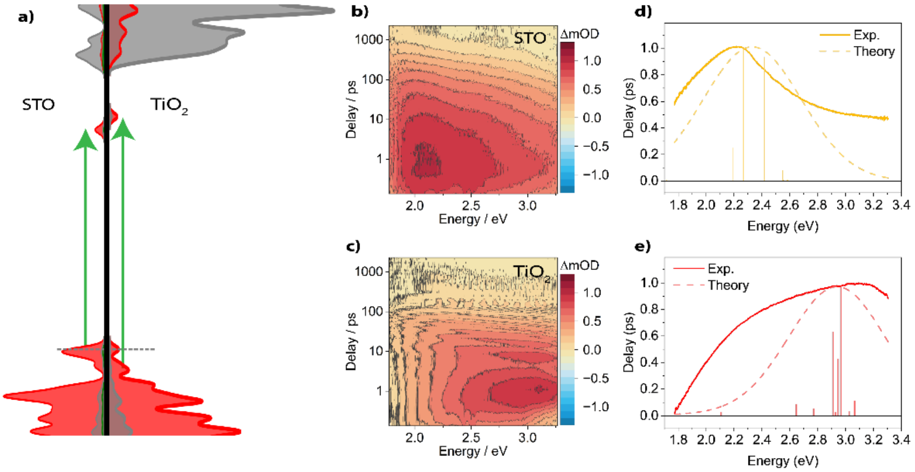

Fig. 1. a) DOS of STO (left) and TiO2 (right), b) Excited state absorption of STO and c) TiO2, d) experimental and theoretical hole polaron spectra of STO and e) TiO2.

In ongoing experiments, we explore how polarization relative to the crystal axes influences the optical response. This includes both electronic transitions and coherent acoustic waves generated by strain pulses from localized lattice distortions, providing insight into the orientation of transition dipole moments, and polaron-induced structural dynamics, respectively.

Together, these studies advance our understanding of the nature and dynamics of hole polarons and their role in OER, thereby contributing to a more complete picture of the overall reaction mechanism.

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This work was supported as part of the Center for Electrochemical Dynamics and Reactions at Surfaces, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0023415.

Selenium as a solar material

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Selenium - the world's first optoelectronic material - is rapidly emerging as a contender for modern solar cells. With its bandgap of ca 1.95 eV and low-temperature processing it is a candidate absorber for indoor solar cells, or as the top-layer in high-efficiency tandem solar cells [1-2]. As a stand-alone solar material, selenium recently surpassed 8% PCE. [3] During the last five years there has been a surge in research in selenium-based solar cells leading to advancements in device structure and performance, but also in fundamental understanding of selenium as a solar material and its (current) limitations [4-6].

We present an overview of selenium as a solar material and give an updated overview of where the field is and where the field is going. In particular, we highlight recent examples of promising device designs, materials processing and advances in understanding of materials parameters.

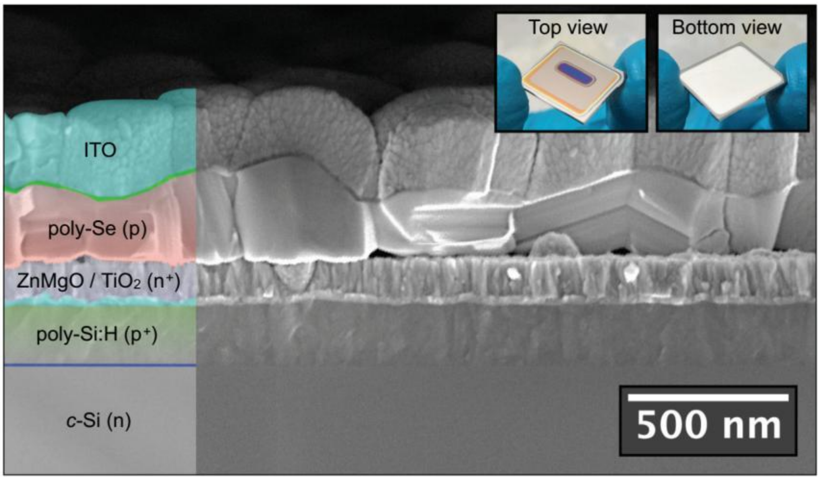

Fig. 1. Cross section of a selenium-silicon tandem solar cell.

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Acknowledgements
The authors gratefully acknowledge support from:
Independant research Fund Denmark (grant 0217-0033B)
The Carlsberg Foundation (fellowship grant CF24-0200)
The Novo Nordisk Foundation (grant NNF24OC0089984)

OC-63

High-performance perovskite solar cells and the modules

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Perovskite solar cells (PSCs) have attracted worldwide attention for its rapidly enhanced power conversion efficiency and facile device fabrication process. There is still a large gap in the stability of device and efficiency of large-area perovskite modules, which seriously lags behind the commercialization process.

We reroute the crystallization pathway of the quasi-2D perovskite films. By controlling the specific adsorption of NH4IxCl1-x additive on different crystal planes, the dynamic preferred growth of (111) plane was deliberately inhibited, and the (202) planes were exposed as secondary nucleation sites to promote the creation of large grains. As the halogen-regulated deprotonation of NH4+ proceeded, (111) crystal planes gradually recovered its growth dominance, and finally formed a vertically-oriented quasi-2D perovskite film with high uniformity, low defect and desired carrier transport. The resultant device achieved an efficiency of 18.5% and a fill factor (FF) as high as 83.4%, which was the highest FF value for quasi-2D PSCs. Then o-PDEAI2 was designed as the passivator to prevent the formation of two-dimensional/three-dimensional (2D/3D) structure and promote the passivation effect. Based on this, we designed 4FPDMAI2 to form 2D/3D heterojunction in the CsPbI3 system to improve their phase stability and the PCEs of the device to 20.13%.

PSCs with the formula FA1-xCsxPbI3 provide an attractive option for integrating high efficiency, durable stability and compatibility with scaled-up fabrication. We visualized the out-of-plane compositional inhomogeneity along the vertical direction across perovskite films and identified the underlying reasons for the inhomogeneity and its potential impact for devices. We devised a strategy using 1-(phenylsulfonyl)pyrrole to homogenize the distribution of cation composition in perovskite films. The resultant p-i-n devices yielded a certified steady-state photon-to-electron conversion efficiency of 25.2% and durable stability. About the modules, we show that incorporating N,N-dimethylmethyleneiminium chloride into the perovskite precursor solution formed dimethylammonium cation and that previously unobserved methyl tetrahydrotriazinium ([MTTZ]+) cation effectively improved perovskite film. The in situ formation of [MTTZ]+ cation increased the formation energy of iodine vacancies and enhanced the migration energy barrier of iodide and cesium ions, which suppressed nonradiative recombination, thermal decomposition, and phase segregation processes. The optimized PSMs achieved a record (certified) PCE of 23.2% with an aperture area of 27.2 cm2, with a stabilized PCE of 23.0%.

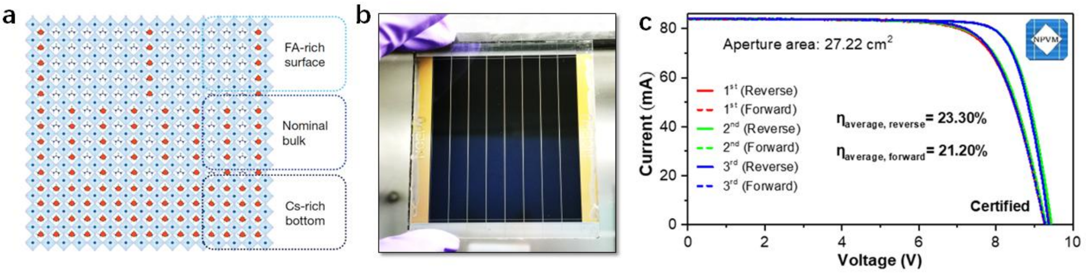

Fig. 1. (a) the distribution of Cs+ in perovskite layer; (b) the picture of perovskite module; (c) the certified J-V curves of perovskite module.

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Acknowledgements

National Natural Science Foundation of China (22279033), the National Key Research and Development Program of China (2023YFB4204502), the 111 Project (B16016), and the Special Foundation for Carbon Peak Carbon Neutralization Technology Innovation Program of Jiangsu Province (BE2022026).

OC-64

When the fate of photogenerated charges matters — classification of heterojunctions in photocatalysis

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Photocatalytic systems designed for various applications often comprise two or more semiconductor components. Such composites are used to achieve an efficient charge separation, more reactive holes or electrons or other additional functionalities. However, proper classification of various heterojunctions formed of semiconductors is often difficult. We have proposed a strategy for correctly elucidating the heterojunction type [1]. It comprises three main steps: (I) the determination of band alignment, (II) the thermodynamic analysis of the interface, and (III) the verification of charge fate and charge transfer kinetics under irradiation (Figure). The experimental techniques appropriate for particular steps, including novel approaches, will be presented, together with their limitations. Following this strategy and methods of spectroscopic [2] and redox [3] characterization of semiconductors it is possible to conduct the analysis, which explores the intricate dynamics of photoinduced charges within correctly classified heterojunctions. Such a strategy gives a more reliable picture than often presented, oversimplified study.

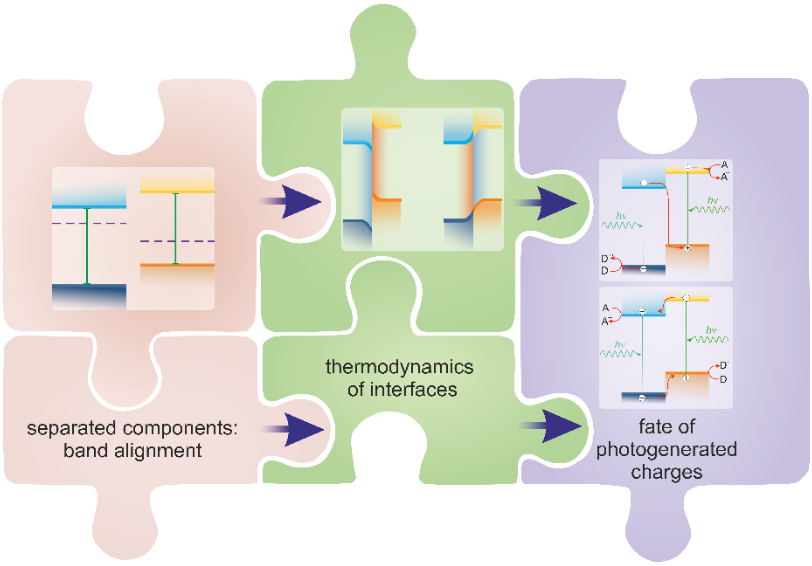

Figure. Determining the type of heterojunction in three consecutive steps: (I) the analysis of band alignment and Fermi levels; (II) the investigation of thermodynamic properties of the interface; (III) the verification of charge fate and charge transfer kinetics under irradiation.

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Acknowledgements

This work was supported by the National Science Centre within the OPUS project (2022/45/B/ST5/04087).

OC-65

Development of an air purification prototype based on photocatalytic filters with biocidal activity

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Respiratory diseases are among the top five risks to public health, causing a large number of deaths per year. Airborne transmission is the main vector of spread and the likelihood of infection is much higher at indoor environments. There is a need to develop innovative sanitary technologies that enable safe environments and help providing preventive devices to contain the transmission of infectious diseases. To this end, we propose new air purifiers based on photocatalytic filters that inactivate viruses and bacteria by oxidative stress, inhibiting their ability to infect cells.

Zinc oxide nanoparticles exhibit antimicrobial activity due to the photoproduction of reactive oxygen species (ROS). However, the recombination rate of photogenerated electron-hole pairs decreases their photocatalytic performance [1]. The use of zinc oxide - cerium oxide nanocomposites has been proposed, since the formation of suitable heterojunctions can reduce the charge recombination processes and in addition, CeO_2 also exhibits inherent redox characteristics that can enhance the generation of such ROS. Since the electronic properties of CeO_2 depend on the types of exposed faces [2], the influence of different ceria morphologies on the behaviour of nanocomposites has been analyzed, observing that the heterojunction with ceria nanocubes, presenting highest proportion of exposed (100) faces, results in higher inactivation. Several characterization techniques (TEM, XRD, Raman, DRIFTS, EPR, XPS/UPS, BET, UV-Vis, fluorescence lifetimes) were used to analyze the structure and morphology of these nanocomposites, as well as their optoelectronic properties. Viral titration assays to evaluate the antiviral effect, as well as inactivation tests of both Gram-positive and Gram-negative bacteria, were performed. Different assays have been designed to elucidate the photocatalytic mechanism and the inactivation process.

In addition, the actual viability of viruses in aerosols has been assessed in a specifically designed chamber. It allows the generation of bioaerosols with viral load, real-time *in situ* monitoring of suspended particles and sampling of bioaerosols, which makes it a powerful tool to study the efficiency of air purification systems. A prototype of the air purifier has been built and tested inside the chamber, using a filter with the most active photocatalyst, obtaining very promising results such as a drop of 7 logarithmic units in the concentration of viruses with infective capacity in the aerosol, and 3 logarithmic units in the viruses physically retained in the filter (Fig. 1c).

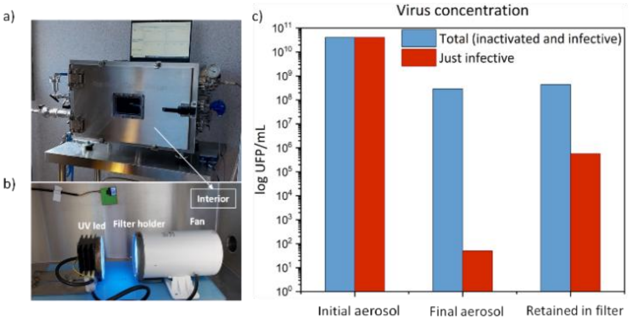

Fig. 1. a) Aerosol chamber (CORINA). b) Interior of CORINA with the photocatalytic air purifier prototype. Inside CORINA, a stable aerosol containing viral load was generated. The aerosol was recirculated through the illuminated photocatalytic filter and subsequently both the virus retained in the filter and the portion remaining in the air or aerosol were analyzed. c) Results of airborne inactivation against phi29: both the concentration of viruses that can continue to infect by viral titration and the total concentration of virus (with and without infective capacity) were analyzed by RT-qPCR.

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Acknowledgements

Project funded by "la Caixa" Foundation, code LCF/PR/HR22/52420032, HR22-00813 and by CSIC PTI+ Salud Global, Nextgeneration EU.

OC-66

Local Photoelectrochemistry and Data Modeling for Properties Extraction of Photoelectrodes

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Recent advances in materials science have opened up great opportunities for the design of heterostructures associating two or more components that could lead to highly efficient photoelectrodes usable for photoelectrochemical (PEC) solar to chemical energy conversion. However, in these heterostructures, any change in morphology or composition will impact all steps of the PEC reaction,[1] making the quest for the best materials and structures a difficult process. Therefore, to assist in the rational design of PEC devices, there is an urgent need for characterization methods to rapidly determine the properties of photoelectrode materials and understand how any structural or physicochemical changes impacts the PEC efficiency. Until now, the optimization of photoelectrodes in terms of material composition, film thickness, or co-catalyst loading is still largely achieved through a trial-and-error approach by synthesizing and analyzing a set of different electrodes, which can be time and resource-consuming.[2]

Here we will present a new analytic approach based on local PEC efficiency measurement using a small light beam as a local probe to scan the surface of photoelectrode with variable properties. We developed an synthesis method that allows the growth of aligned TiO_2 nanotubes (NTs) with length increasing gradually from 0 to 15 µm, on a single electrode.[3] This method was employed to synthesize TiO_2-NTs with variable length but also doped TiO_2-NTs with cations (Nb, Ta) and/or nitrogen.[4] The optimal thickness of TiO_2, M-doped, N-doped, and (M:N) codoped TiO_2-NTs (with M= Nb or Ta) for photoelectrochemical (PEC) water splitting was determined, in one step, through local PEC analysis of the electrodes with variable thickness of the SC material. The external quantum efficiency as a function of the NTs film thickness was measured by scanning photocurrent microscopy (SPCM) under UV and visible light to scan the surface and locally trigger the oxygen evolution reaction. The results provide the optimal NT layer thickness for each type of doped TiO_2-NTs and demonstrate that if the (M:N) codoped TiO_2-NTs have the best activity under visible light, the optimal layer thickness is reduced compared to TiO_2 or M:doped TiO_2-NTs. Additionally, by fitting the data with a model that incorporates charge carrier transfer and light absorption mechanisms in the film, it becomes possible to evaluate in operando the interfacial charge transfer, absorption coefficient, or majority carrier mean path which are important properties of semiconducting materials for PEC applications.[5] The extraction of these parameters was used to correlate the behaviours of M-doped, N-doped, and (M:N) codoped TiO_2-NTs with the changes of electronic conductivity and light absorption depending on the doping species.

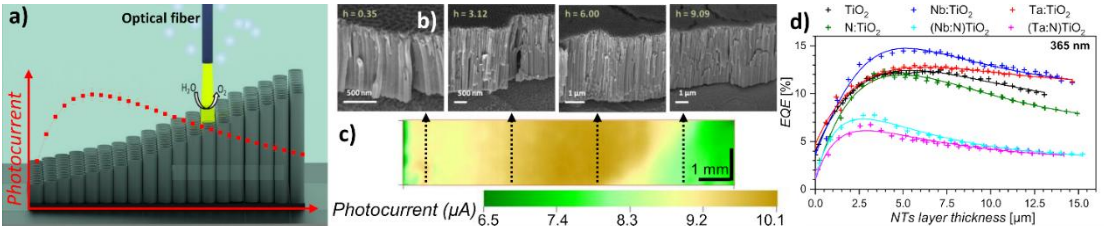

Figure 1: a) Principle of SPCM on NTs gradient. b) SEM images of TiO_2-NTs with variable lengths obtained on a single electrode. c) 2*10 mm SPCM photocurrent mapping of the electrode.[3] d) experimental data of EQE vs NTs length for doped TiO_2-NTs and fitted curves.[5]

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ITI HiFunMat is acknowledged for S.V. scholarship. This research and the Ph.D. of F.G. were funded by the ANR through the ANR BAGETE (ANR-16-CE05-0001-01) project.

OC-67

Correlation of cyclic voltammetry and impedance spectroscopy models on TiO_2 photoelectrodes

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Photoelectrochemical water splitting is considered a future alternative to classical electrolysis for green hydrogen production and solar energy storage. Photoelectrode materials are typically characterized by electrochemical techniques, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). A quantitative understanding of experimental data has been approached by means of physical models that derive from electrical circuit analogues. While EIS models are quite widely used and have been implemented in commercial software [1], CV modelling has not been commonly applied since the original work by Fabregat-Santiago et al. [2, 3]. Therefore, the consistency between models still needs to be clarified.

In this communication, we analyse a series of TiO_2 photoelectrodes having increasing layer thickness and different TiO_2 particle constituents, by means of CV in a well-defined potential window, and EIS at different potentials inside that window (Fig. 1).

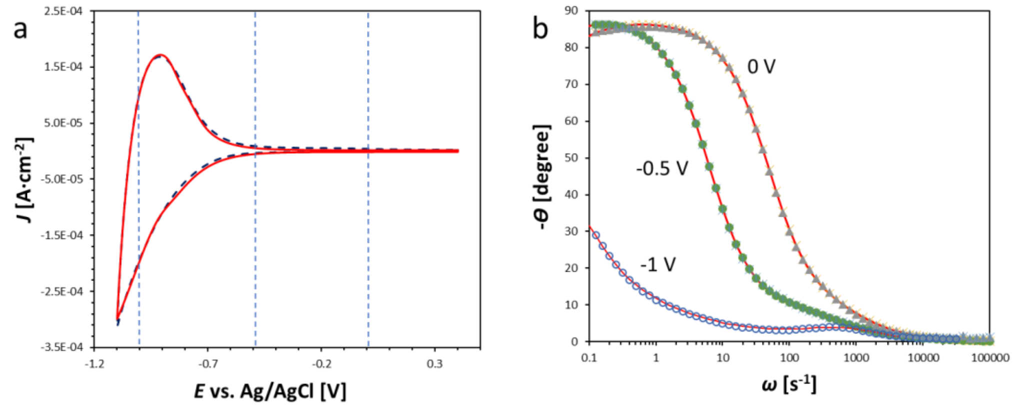

Fig. 1. Electrochemical analysis in the dark of a TiO_2 photoelectrode, showing model fittings (solid lines): a) CV, and b) Phase Bode plot (EIS) at three potentials. Electrolyte: 0.1M Na_2SO_4 + 0.1M EDTA.

We compare the results of data modelling from both CV and EIS techniques. Qualitatively, both models together provide a coherent physical interpretation of phenomena taking place in the electrode. Quantitatively, they yield consistent values for the fitting parameters, except for large cathodic potentials (-1 V vs. Ag/AgCl). Specifically, when the capacitance is calculated by fitting EIS data, it exceeds that from CV at equivalent measuring potentials. Such a difference is a consequence of intrinsically distinct local conditions during CV and EIS measurements: voltage in EIS is kept around a fixed negative value for a much longer time than in CV, which favours charge accumulation at the solid-electrolyte interphase. The difference between models is found to depend on the TiO_2 material origin and electrode thickness. Finally, the activity of the prepared specimens as photoanodes is registered under light irradiation: the highest photocurrents are obtained on the TiO_2 material exhibiting the smallest divergence between CV and EIS model parameters.

Our work thus contributes to a deeper fundamental comprehension of physical mechanisms taking place at semiconductor photoelectrodes.

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Financial support from Spanish MCIN/AEI/10.13039/501100011033 and “ERDF A way of making Europe” under project grant PID2022-139671OB-I00, as well as by the Gobierno de Aragón (DGA) under project T03_23R (Grupo de Investigación Reconocido) is acknowledged.

Bismuth vanadate coatings produced by magnetron sputtering for water treatment: antimicrobial activity, photocatalytic efficiency, and toxicity assessment

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The availability of sufficient and safe drinking water is a critical public health issue. One of the United Nations (UN) goals Sustainable Development Goals is to ensure universal access to water and sanitation by 2030. Heterogeneous photocatalysis is an Advanced Oxidation Process (AOP) that has been described as a suitable technology for enhancing safety in water treatment regarding disinfection. However, this technology has faced several challenges, including recovery, separation, and recycling of the photocatalyst, thus hindering large-scale application. Another concern is the toxicity caused by the persistence of these particles in the treated matrix.

Among the deposition techniques available, magnetron sputtering stands out as a relatively simple, versatile, and easily scalable vacuum-based method used to deposit various materials onto different supports. This physical deposition technique offers a number of obvious advantages, such as high productivity, ability to control coatings thickness and particle size and lack of hazardous precursors, when compared to chemical methods.

Here, reactive magnetron sputter deposition was utilised for production of bismuth vanadate ($BiVO_4$). This material has attracted significant interest due to its low band gap, non-toxicity, and corrosion resistance, resulting in excellent photocatalytic activity in the degradation of organic pollutants under visible light irradiation. The presented work is the first systematic study of how deposition parameters may affect the properties of bismuth vanadate coatings. Thus, the present work aims to address the observed gap and investigates how operational parameters for $BiVO_4$ thin film production by magnetron sputtering influence their chemical, physical, and optical properties and, consequently, their photocatalytic activity.

A design of experiments Taguchi L9 array was first used to determine the optimum deposition conditions to maximise photocatalytic properties of $BiVO_4$. The samples were characterized and through photocatalytic assessment, the $BiVO_4$ optimal production condition was determined as being 4 mTorr of pressure, 100 kHz pulse frequency, 90% duty cycle, and 2 h deposition time. The $BiVO_4$ antimicrobial proprieties were assessed following the British Standard ISO 27447:2009 with E. coli. Antimicrobial activity was observed under visible light, resulting in values under the detection limit (<LD) within 24h. The material showed activity in the dark, achieving values <LD within 48h. According to ISO 10993–5:2009, different cytotoxicity levels in humane intestinal cells were observed within the tested concentrations range. This antimicrobial activity is unprecedented, indicating a significant opportunity for advancement in disinfection and offering a safe alternative to conventional water treatment.

OC-69

Distinct Cesium Adsorption Mechanisms of Prussian Blue Analogues with Transition Metals

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Radioactive cesium (^{137}Cs) remains a serious environmental threat due to its long half-life and high mobility. Among various adsorbents, Prussian blue analogues (PBAs) have shown remarkable selectivity and efficiency in Cesium (Cs$^+$) removal. Over the past several years, our research has systematically advanced PBA-based technologies for Cs$^+$ adsorption, evolving from PB-embedded nanofibers to photo-responsive and seawater-applicable systems. Initial developments involved PB embedded in PAN nanofibers and PB-TiO$_2$ composites that exhibited photocatalytic enhancement under UV irradiation [1]. This was followed by electrochemical adsorption/desorption systems using PB on carbon nanofibers [2], and PB membranes formed with carboxymethyl cellulose nanofibrils [3]. More recently, NiFe-PBAs showed light-induced Cs$^+$ uptake enhancement [4], while NiFe incorporated into carbon nanofibers enabled electrochemically controlled adsorption and desorption [5]. Additionally, NiFe embedded in alginate hydrogel matrices demonstrated efficient Cs$^+$ removal and reusability, even in seawater environments [6].

This study explores the influence of different transition metal ions (Co, Cu, Fe, Mn, Ni, Zn) on the Cs$^+$ adsorption behaviour of PBAs. The PBAs were synthesized and characterized with respect to specific surface area, ion exchange capacity, lattice parameters, and defect levels associated with coordinated water molecules. **The adsorption mechanisms varied significantly depending on the metal composition (Fig. 1). CoFe and FeFe PBAs exhibited dominant K$^+$/Cs$^+$ ion exchange due to higher potassium content, while CuFe and MnFe PBAs, rich in defect sites, primarily facilitated H$^+$/Cs$^+$ exchange. Notably, NiFe and ZnFe PBAs demonstrated enhanced Cs$^+$ uptake under light irradiation, attributed to their photo-responsive nature that induces electron-mediated Fe(III) to Fe(II) reduction, thereby boosting adsorption efficiency.**

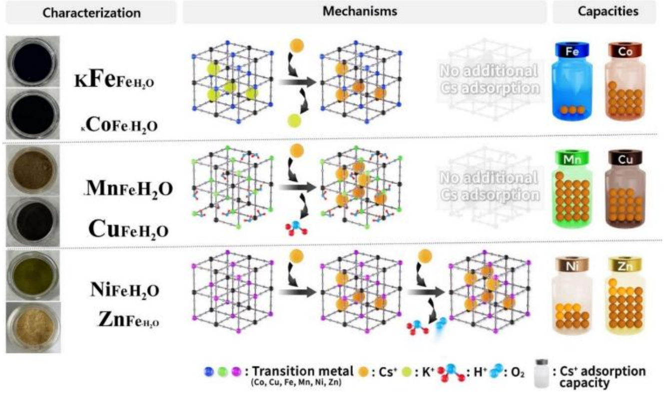

Fig. 1. Schematic highlighting the characterization, Cs$^+$ adsorption mechanisms, and capacities of various PBAs.

Additionally, filter-type PBAs were evaluated for their performance in real seawater samples, suggesting practical applications in rapid pre-treatment for environmental monitoring. The adsorption behaviour revealed a strong dependence on the type of transition metal, highlighting the importance of metal selection in designing effective PBA-based decontamination systems.

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This work was supported by the Nuclear Safety Research Program through the Korea Foundation Of Nuclear Safety(KoFONS) using the financial resource granted by the Nuclear Safety and Security Commission(NSSC) of the Republic of Korea. (No. RS-2023-00231329).

Highly efficient photocatalyst based on layered LDH/g-C_3N_4 heterojunction for degradation of pharmaceuticals products in water

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Nowadays, pollution of water is a relevant problem worldwide. Among the possible contaminants, emerging contaminants are each day more studied, and they include several synthetic or natural substances, such as pharmaceuticals and personal care products, which before having not been considered as that. The presence of many of these contaminants in water do not produce changes in its appearance, making water pollution imperceptible; however, damage to health and ecosystems can be reflected in the short or medium term. Among emergent contaminants found in water Ibuprofen, an anti-inflammatory and one of the most used analgesics is frequently reported. Since under thermal decomposition, it releases acrid smoke, a recommended route to eliminate this pollutant water is applying Advanced Oxidation Processes (AOPs), and particularly photocatalysis. On the other hand, the use of heterojunctions as photocatalyst has been reported to accelerate redox reactions by increasing the active radical species production which helps in degradation. Based on that above described, in this work we present the results of the photodegradation and mineralization of ibuprofen in water using as photocatalyst an heterojunction based on calcined LDH and gC_3N_4. High level of photodegradation and a very close mineralization (formation of CO_2 and H_2O) were reached under a low intensity lamp of 365 nm UV light irradiation.

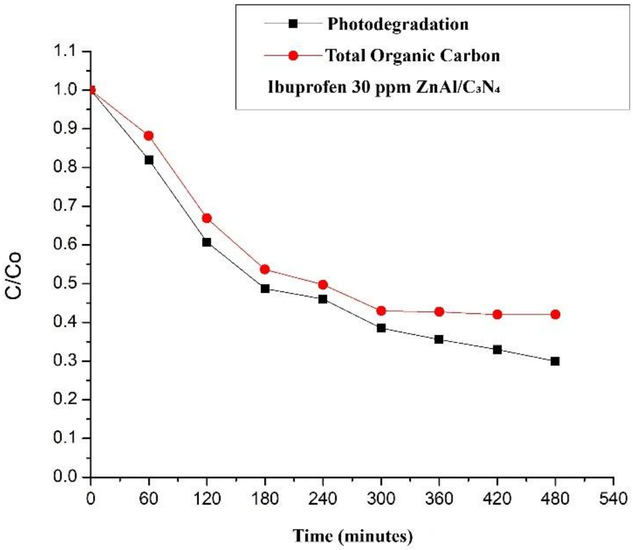

Fig. 1. Ibuprofen degradation and mineralization using LDH/g-C_3N_4 heterojunction as photocatalyst.

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Acknowledgements

Authiors thank to 285711 CB CONAHCyT, 20251220 SIP projects for economical support to this work. D. León thanks to SECIHTI and BEIFI (IPN) for scholarship.

OC-71

Photolytic and photocatalytic degradation of lomefloxacin by a Z-scheme photocatalytic system: mechanism and kinetics study

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As a fluoroquinolone (FQ) antibiotic, lomefloxacin (LOM) is widely used to treat bacterial infections due to its broad-spectrum of antimicrobial activity. However, despite its effective use, it can lead to serious symptoms such as nausea, diarrhea, abdominal pain, and dizziness when accumulating in human and animal bodies over time [1]. It may also promote the growth of antibiotic-resistant bacterial strains [2]. Photolysis and photocatalysis are two of the common ways to remove the LOM residue in aquatic ecosystems. Compared to photolysis that may result in the formation of intermediate by-products that could still pose ecological risks, photocatalysis can lead to the breakdown of LOM into non-toxic, biodegradable products, thus minimizing the potential environmental hazards. Among various photocatalysts, Z-scheme heterogeneous photocatalyst has demonstrated its effectiveness due to its enhanced charge separation, strong redox potential, and wide spectral absorption [3]. The Z-scheme photocatalytic system allows for more flexibility in designing photocatalysts by combining different semiconductors with complementary properties.

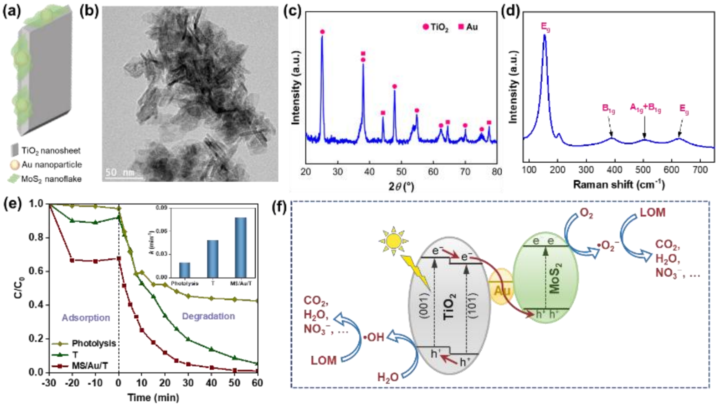

Fig. 1. (a) MS/Au/T catalyst's structure, (b) TEM image of MS/Au/T, (c) LOM degradation performance by photolysis and photocatalysts, and (d) photodegradation mechanism of LOM by MS/Au/T.

Herein, we fabricated an edge-connected 2D/2D $MoS_2/Au/TiO_2$ (MS/Au/T) Z-scheme photocatalyst for effective removal of LOM. In the designed system, TiO_2 nanosheets (T) were first synthesized. Au nanoparticles (NPs) were then deposited on the edges of TiO_2. MoS_2 was finally grown on Au NPs and the edges of TiO_2 (Fig. 1a). The morphology of MS/Au/T was studied by TEM (Fig. 1b). The structure of MS/Au/T was investigated by XRD and Raman. As shown in Fig. 1(c), several typical diffraction peaks at around 25.1°, 38.1°, 47.9° and 75° are indexed to the (101), (004), (200), and (215) crystal planes of anatase TiO_2 [4], respectively. The diffraction peaks at around 38.1°, 44.3°, 64.4°, and 77.5° can be assigned to the (111), (200), (220), and (311) crystal planes of Au [4]. The Raman peaks at 143, 392, 511 and 632 cm^{-1} in Fig. 1(d) could be assigned to E_g, B_{1g}, A_{1g} and E_g vibration modes of anatase TiO_2, respectively. However, no MoS_2 signal was detected in both XRD pattern and Raman spectrum due to its amorphous structure and poor crystallinity. The degradation performance of LOM by photolysis and photocatalysis was then compared. As shown in Fig. 1(e), the photolytic removal of LOM remained unchanged after 30min, illustrating an incomplete degradation behaviour. Photocatalytic degradation by pristine T and MS/Au/T guaranteed complete removal of LOM within 60 min. Especially, the Z-scheme MS/Au/T exhibited the largest pseudo 1st-order rate constant, demonstrating its effectiveness in LOM removal. The photodegradation mechanism by Z-scheme MS/Au/T was also investigated, as shown in Fig. 1(f).

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This work was supported financially by Khalifa University Emerging Science & Innovation Grant (ESIG-2023-002) and Research & Innovation Grant (RIG-2023-054).

OC-72

MOF-semiconductor interaction - How the type of the connection in the heterostructures may control mechanisms of photoinduced processes?

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Development of efficient and stable systems utilizing accessible and renewable energy sources is still one of the biggest scientific challenges of present days. One of the strategies for the development of the materials exhibiting high charge carrier generation and separation efficiency is the formation of the heterostructures. Recently, hybrid materials composed of MOFs and semiconductors have gained much attention due to their high photocatalytic and photoelectrochemical activity, significant stability, and, what is most important, enormous chemical and structural diversity of MOFs components.

Although, a great deal of such hybrid systems have been developed, the effects occurring at the MOF-semiconductor interface are still not well understood and systematic research on this matter is lacking. The improved photoactivity of such composites is mainly attributed to electron transfer between the excited MOF and the conduction or valence band of semiconductor. The consequences of strong interaction of organic linkers present in the MOF structure with the surface of semiconductors are usually ignored, even though there are several works showing that chemisorption of simple organic molecules (including terephthalic acid, a well-known MOFs' ligand) can significantly improve the photoactivity of semiconductors [1, 2, 3].

In our studies we developed a series of hybrid materials in which the MOF structure was synthesized on the surface of bare titania and titania pre-modified with monolayer of various organic and inorganic compounds, including ligands present in the MOF structures. It turned out, that the photochemical and (photo)physical properties of the composites strongly depend on the type of linkers occurring at the MOF-semiconductor interface (Figure 1). The nature of the modifiers present at the semiconductor surface determines not only the efficiency of the MOF synthesis but also has a huge impact on the mechanisms of light-induced processes and interactions between the components. In some cases, were bare titania is covered with MOF crystals, there may even be an advantage of photosensitization resulting from the interaction of linkers present in the MOF structure with the semiconductor over the sensitization resulting from light-induced electron transfer between the excited MOF and the semiconductor.

In the present work the impact of type of the contact between MOF and semiconductor components and their interaction on the density of acceptor states of semiconductor and spectroscopic, (photo)electrical, and (photo)electrochemical properties of hybrid materials will be presented. In particular, the mechanisms of photoinduced processes and the kinetics of interfacial charge transfer processes will be thoroughly discussed.

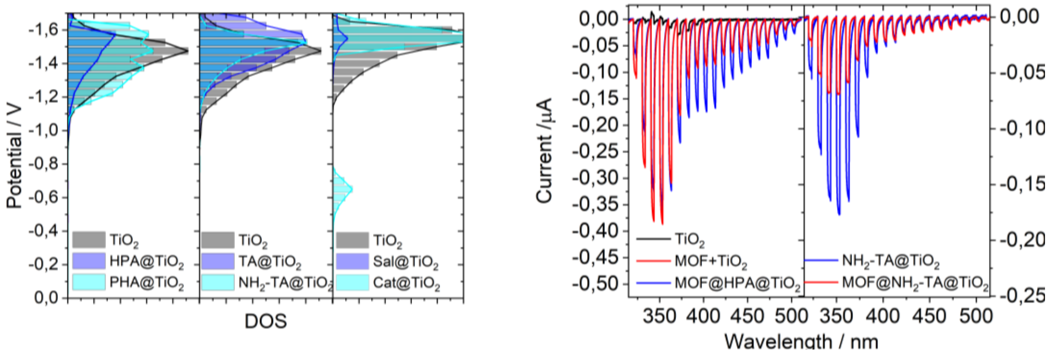

Fig. 1. DOS (left) and photoelectrochemical action spectra (right) of the TiO_2 surface-modified with HPA (hexylphosphonic acid), PHA (6-phosphonohexanoic acid), TA (terephthtalic acid), NH_2-TA (2-aminoterephthtalic acid), cat (catechol), sal (salycylic acid), and MOF (NH_2-MIL-125-Ti).

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Acknowledgements

This work has received financial support from the National Science Centre within the project number 2017/26/D/ST4/00642 (SONATA 13).

Flash oral & poster communications

F-1/P-1

Photocatalytic Degradation of Tetracycline in Wastewater Using Ti-$LaFeO_3$ Foam/Powder

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Pharmaceuticals and personal care products are regularly introduced into water systems. Among them, tetracycline (TC), a commonly used antibiotic, poses significant environmental risks due to its persistence and resistance to natural breakdown. Its removal is difficult and demands advanced treatment technologies. The ongoing issue of water contamination underscores the urgent need for innovative approaches. The objective of this study is to eliminate water contaminants like tetracycline using catalysts in both powder and foam forms, under conditions with and without light.

$Fe(NO_3)_3 \cdot 9H2O$, $La(NO_3)_3 \cdot 6H_2O$, ($C_6H_8O_7$) and TiO_2 P25 were used. The β-SiC alveolar foams were used as 5 cm (d) × 2 cm (h) disks.

The as-made Ti-LaFeO3 was synthesized using a modified sol-gel Pechini method [1]. Ti-$LaFeO_3$ catalysts were made by carefully adding the mixture to β-SiC foam disks using drop method. Instead of making the catalyst separately, we created it directly on the foam's surface by dripping the starter solution onto it. The foam was dried at 80°C between applications and then overnight. Calcination followed a 5°C/min heating rate, with holds at 600°C for 2 hours and 800°C for 2 hours [2].

Figure 1 illustrates the impact of different oxidant systems on tetracycline (TC) degradation using Ti-$LaFeO_3$ and Ti-$LaFeO_3$-SiC under both dark and solar conditions. The Solar/Ti-$LaFeO_3$-SiC/PMS system demonstrated the highest efficiency, emphasizing the strong synergy between PMS, solar energy, and the catalyst. In contrast, Ti-$LaFeO_3$/PMS in the dark showed only moderate performance, while Solar/Ti-$LaFeO_3$/H_2O_2 was slightly less effective than the PMS-based system. The lowest degradation occurred with Ti-$LaFeO_3$/H_2O_2 in the dark, likely due to limited activation without sunlight. These results underscore the critical role of oxidant choice and solar irradiation, with the Solar/Ti-$LaFeO_3$-SiC/PMS system emerging as a highly promising method for efficient TC removal in wastewater treatment.

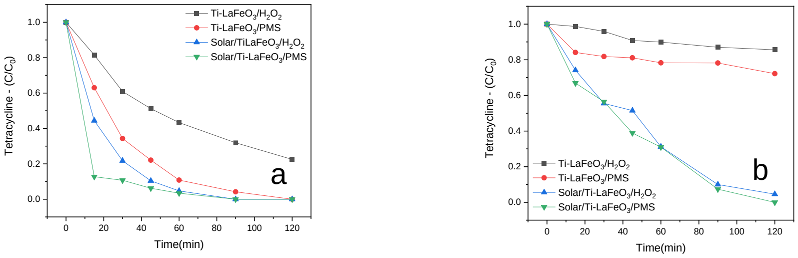

Fig.1. TC degradation in Ti-$LaFeO_3$/PMS and Ti-$LaFeO_3$/H_2O_2 processes in presence and absence of solar light (pH = 3, [TC] = 10 mg/L, a) [Ti-$LaFeO_3$] = Foam, [PMS] = 2.2mM, [H2O2] = 2.2mM b) [Ti-$LaFeO_3$] = Powder, [PMS] = 0.55mM, [H2O2] = 1.1mM).

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F-2/P-2

A new approach for developing highly efficient TiO_2 and $SrTiO_3$-based photocatalytic films

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One of the most important factors affecting the efficiency of photocatalytic processes is the ability to separate photoinduced charges (electrons and holes) efficiently. Increasing the charge separation and thus reducing the recombination processes can be achieved, for example, by synthesizing titanium(IV) oxide or strontium titanate crystals with controlled facet exposition. The presence of different potentials on the surface of such crystals causes the segregation of photogenerated charges into specific crystallographic facets. As a result, the exposed crystal planes are enriched in holes or electrons and are preferred in reduction or oxidation processes [1, 2]. Another approach that could promote better separation of photoinduced charges is the development of photoactive coatings with variable composition (also with gradient composition). This approach can create heterojunction systems. Photocatalytic coatings with variable composition should provide better separation of oxidation and reduction processes and, thus, higher efficiency of photocatalytic reactions. Such coatings can be used in oxidation reactions (e.g. degradation of contaminants) and reduction reactions (e.g. transformation of organic compounds).

In this work, a series of films with different compositions based on titanium(IV) oxide and strontium titanate were synthesized. Several techniques, such as the *liquid phase deposition* (LPD) method, sol-gel spin-coating, etc., were used. Examples of the obtained composite layers are presented in Figure 1. The crystallinity and phase compositions of films were explored by XRD, Raman, UHR SEM, EDS and ToF-SIMS. The photoelectrochemical and photocatalytic activity were studied *inter alia* in water and methanol oxidation.

The impact of the type and composition of film for photocatalytic activity will be presented and discussed.

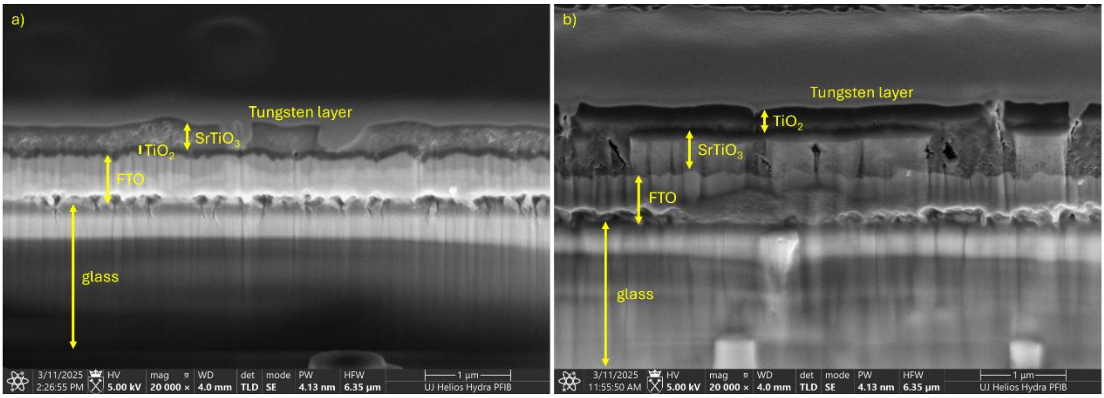

Fig. 1. SEM images of the cross-section of $SrTiO_3@TiO_2$ (a) and $TiO_2@SrTiO_3$ (b) films on an FTO glass substrate.

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Acknowledgements

This work was supported by the National Science Centre within the OPUS23 (2022/45/B/ST5/04087) project.

F-3/P-3

Advanced Oxidation Processes: a powerful tool for nanoplastics removal in water

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Small plastic debris are ubiquitously present in coastal and aquatic ecosystems, primarily transported by wind and water currents. In recent years, nanoplastics (NPs, <1 µm) have raised significant concerns due to their potential risks to both the environment and human health [1]. However, wastewater treatment plants are ineffective at removing NPs, as their size is typically smaller than the pore size of conventional filters, and their colloidal behaviour further limits removal by other treatment processes. To address this challenge, advanced treatment technologies have emerged as promising solutions for NP elimination, with advanced oxidation processes (AOPs), particularly photocatalysis, being notable methods for degrading NPs in water.

The primary aim of this study is to evaluate the ability of different heterogeneous AOPs, and in particular photocatalysis, to mineralize NPs, and to assess the impact of various parameters on NPs mineralization [2]. Immobilizing the catalysts is necessary to implement the photocatalytic tests and obtain performance indicators. Therefore, macroscopic 3D silicon carbide (SiC) foams have been used as photocatalyst supports due to their high chemical and thermal stability, along with their open-cell structure that facilitates irradiation of the reactor core [3]. A stepwise dip-coating technique with final thermal annealing at 550°C was used to obtain a uniform TiO_2-P25 coating on the 3D SiC substrate. The TiO_2-P25/SiC foam was placed in a quartz beaker-type photoreactor in contact with stirred aqueous NPs dispersions. NP model materials of polystyrene (NPs PS) were synthesized at IPREM for this project, diluted to have an initial Total Organic Carbon (TOC) content of 10 mg/L. At regular intervals during the tests, the suspension was sampled and analysed for TOC without filtration. A span of physico-chemical techniques were used to get information on the evolution of the NPs PS and the products formed.

Figure 1 demonstrates that control experiments, including the catalyst in the dark, bare SiC foam, or photolysis conditions, did not lead to any degradation of NPs. In contrast, under UV-A irradiation (λ = 365 nm at 34 W/m²), significant degradation and mineralization of the NPs occurred using the TiO_2-P25/SiC photocatalyst. Nearly 90% mineralisation of the PS NPs was achieved after 8 h of irradiation. The addition of peroxymonosulfate (PMS) accelerated the process, achieving 90% mineralisation within 4 h. Results will also show the influence of various parameters, including particle size and surface functionality of NPs, irradiation type and power, and catalyst.

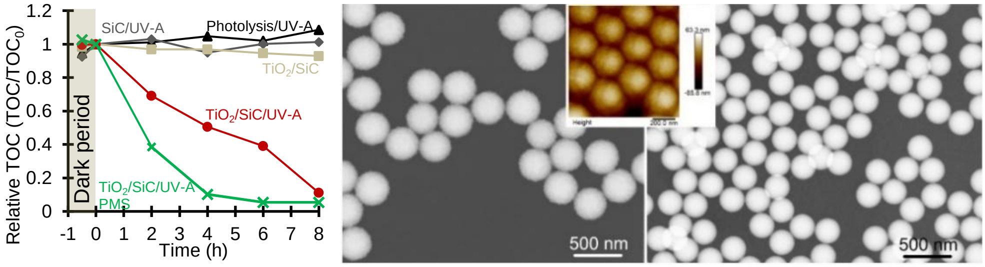

Figure 1. (Left) Adsorption (dark), photolysis and UV-A photocatalytic (with and without PMS) mineralisation of PS NPs in water on macroscopic TiO_2-P25/SiC foams (Calibrated size of PS NPs of 298 nm). STEM images, done at IPREM, of calibrated PS NPs of 422 nm (middle with AFM image in insert) and 298 nm (right).

Preliminary results indicate that the photocatalytic mineralisation of PS NPs in aqueous solution under UV-A irradiation using TiO_2-P25/SiC foams and PMS is highly effective. Further optimization is necessary, including the development of novel photocatalysts and the elucidation of potential degradation mechanisms.

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This work is supported by the French National Research Agency in the frame of the project AOPNANOP (ANR-22-CE04-0011). This work of the Interdisciplinary Institute HiFunMat, as part of the ITI 2021-2028 program of the University of Strasbourg, CNRS and Inserm, was supported by IdEx Unistra (ANR-10-IDEX-0002) and SFRI (STRAT'US project, ANR-20-SFRI-0012).

F-4/P-4

$BaTiO_3$–TiO_2 Heterojunction Thin Films via LPD as Photocatalysts for Oxidation

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Enhancing the efficiency of photocatalytic and photoelectrocatalytic reactions on photoactive coatings is an area of active research currently. A key challenge is the effective separation of photoinduced charge carriers (electrons and holes) to minimize recombination losses. One of the strategies to prevent these processes is the synthesis of heterojunctions.

In this work, we focused on the fabrication of heterojunctions composed of well-known and highly active titanium dioxide (TiO_2) and barium titanate ($BaTiO_3$). Barium titanate was selected due to its high versatility and efficiency as a photoactive material. It offers several key advantages, including low cost, non-toxicity, excellent chemical stability, and unique ferroelectric properties. Its ability to form effective composites with other materials further enhances its photocatalytic performance, making it particularly promising for environmental applications such as wastewater treatment and the degradation of organic pollutants[1].

Liquid phase deposition (LPD) is the preferred synthesis method and offers numerous advantages, including cost-effectiveness, simplicity, and the ability to produce high-quality films without vacuum conditions.[2] The photocurrent measurements revealed that the $BaTiO_3$-TiO_2 heterojunction exhibits, inter alia, superior performance compared to TiO_2 film in 0.1 M KNO_3. This effect becomes more evident when methanol is used as a doubling agent.

This study aims to develop photoactive coatings with a gradient composition to enhance the separation of photoinduced charge carriers.

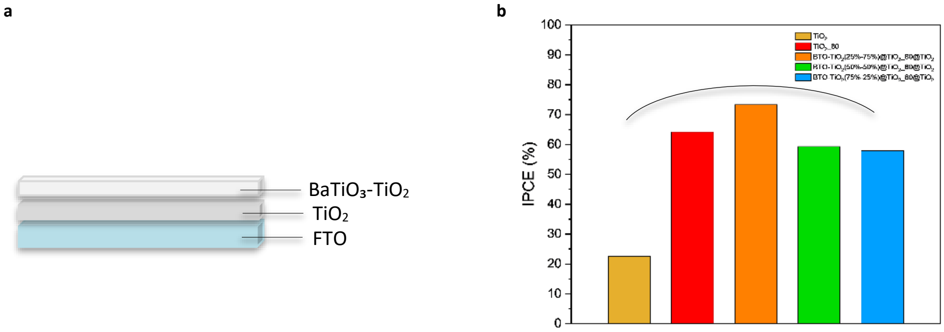

Fig. 1.a. Structure of the photoelectrode **b.** IPCE measurements of TiO_2 and $BaTiO_3$-TiO_2 heterojunction thin films in 0.1 M KNO_3 + CH_3OH at 350 nm, 1 V

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Acknowledgements

This work received financial support from the National Science Centre (2022/45/B/ST5/04087).

F-5/P-5

Covalent Organic Frameworks for Solar-Driven Hydrogen Peroxide Production from Water and Air

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Hydrogen peroxide (H_2O_2) is a vital chemical used in disinfection, chemical synthesis, and environmental remediation. However, conventional production methods, such as the anthraquinone process, rely on fossil-derived organics and noble-metal catalysts, generate chemical waste, and are energy-intensive. Alternative routes, including electrochemical synthesis and direct H_2/O_2 reactions, face challenges like high costs, catalyst degradation, and safety risks. Thus, developing a sustainable and efficient approach for H_2O_2 production is crucial nowadays. In this sense, covalent organic frameworks (COFs) have emerged as promising free-metal photocatalysts due to their tunable porosity, high surface area, and excellent stability. Their π-conjugated structures enable efficient light absorption and charge separation, making them ideal for photocatalysis applications [1].

In this study, we synthesized three novel COFs by coupling 1,10-phenanthroline-2,9-dicarbaldehyde (PTA) with three amine-based linkers: 4,4',4''-(1,3,5-triazine-1,3,5-triyl)trianiline (TTT), 5'-(4-aminophenyl)-[1,1':3',1''-terphenyl]-4,4''-diamine (TAB), and benzene-1,3,5-tricarbohydrazide (THB), forming PTA-TTT, PTA-TAB, and PTA-THB, respectively. The photocatalytic performance of these materials was evaluated using a home-made glass reactor with a removable quartz window at the top and a 300 W Xenon lamp ($\lambda > 400$ nm) as the light source. Standard conditions included 5 mg of catalyst in 30 mL of deionized water, stirred at 300 rpm at 20 ºC under open-air conditions. H_2O_2 production was quantified using the colorimetric potassium titanium oxalate method, with UV-Vis spectroscopy at 379 nm [2].

Preliminary results indicate that all three COFs exhibit catalytic activity, with PTA-TAB, PTA-TTT, and PTA-THB achieving productivities of 1267, 930, and 523 µmol H_2O_2 g_{cat}^{-1} over 24 h, respectively. Despite PTA-THB having the highest initial rate (165.8 µmol H_2O_2 g_{cat}^{-1} h^{-1}), slight deactivation was observed over time, whereas PTA-TAB maintained stability, making it the most promising candidate. Recyclability tests confirmed PTA-TAB robustness, with minimal productivity loss over three cycles (1167 → 1087 → 930 µmol H_2O_2 g_{cat}^{-1}). Thus, the long-term performance, PTA-TAB demonstrates strong stability and efficiency, making it a promising material for green chemical applications and industrial processes. These findings highlight the potential of COFs as efficient, metal-free, and sustainable photocatalysts for H_2O_2 production, utilizing only water, air, and visible light. More information regarding reaction mechanisms, photophysical properties of the COFs and optimization of the reaction conditions will be investigated.

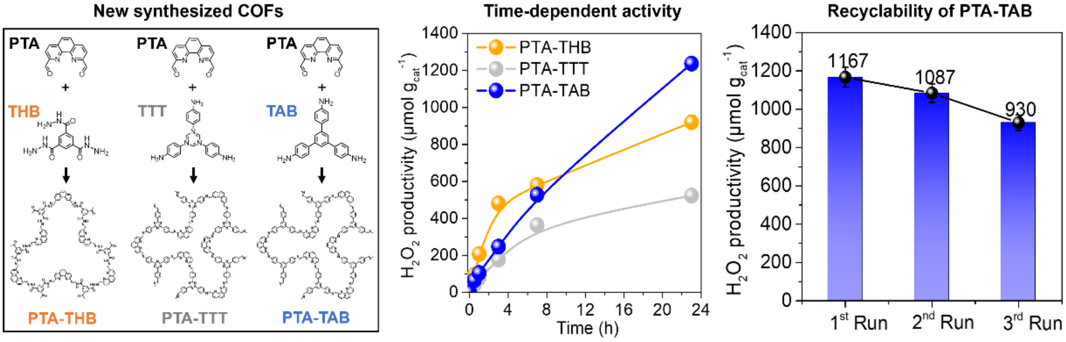

Fig. 1. Chemical structure of the new COFs studied in this work. Evaluation of H_2O_2 photosynthesis under water and air atmosphere of the COFs. Stability of PTA-TAB over three consecutive cycles of reaction for 24h/cycle.

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F-6/P-6

Dehalogenation reaction over co-catalyst loaded carbon nitride photocatalysts

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Aromatic chlorides are typical pollutants causing various environmental problems due to their persistence. In most cases, incineration is used for treatment of aromatic chlorides. However, this approach requires substantial energy and converts valuable aromatic compounds to carbon dioxide and water. To address this issue, we focused on the dechlorination reaction and recovery of aromatics using photocatalysts. We have reported that the dechlorination of chlorobenzene to benzene proceeds efficiently at room temperature and atmospheric pressure using a titanium dioxide photocatalyst under UV light irradiation [1,2]. Recently, carbon nitride (C_3N_4) photocatalyst has attracted attentions having an advantage in an element strategy [3]. In this study, we investigated dechlorination of *p*-chlorotoluene (PCT) using metal co-catalyst (M) loaded C_3N_4 (M/C_3N_4) photocatalyst.

C_3N_4 was prepared by calcination of a mixture of urea (4 g) and melamine (36 g) in an alumina mortar at 450°C for 4 h. The C_3N_4 was washed with an aqueous sulfuric acid solution (pH= 4). Various co-catalysts (M= Pd, Pt, Rh, Ag and Au) at 1.0 wt% were loaded on C_3N_4 by using a photodeposition method. M/C_3N_4 (50 mg) was suspended in 80 vol% 2-propanol (5 cm^3) containing PCT (100 μmol) in a test tube. After the test tube was sealed with a rubber septum, the gas phase was replaced with Ar. The mixture was irradiated with light from a high pressure mercury lamp (Koike, Hyogo, Japan, λ> 300 nm). The compounds in the gas and liquid phases after the reaction were determined by gas chromatography.

Table shows the amount of toluene produced after 0.5 h in the dechlorination reaction of PCT over M/C_3N_4 photocatalyst, indicating that the highest yield of toluene was obtained when Pd/C_3N_4 was used. The amounts of PCT adsorbed on C_3N_4 and M/C_3N_4 were determined in the dark and the differences in the adsorption amounts between of C_3N_4 and M/C_3N_4 are also shown in Table, indicating that Pd showed the largest adsorption ability of PCT. The temperature dependence of the reaction rates of Pd/C_3N_4 and Pt/C_3N_4 was investigated. The activation energies of Pd/C_3N_4 and Pt/C_3N_4 were similar, while the frequency factors (*A*) were determined to be 2.43×10^3 s^{-1} and 6.51×10^2 s^{-1}, respectively. The difference in the activity for the dechlorination over M/C_3N_4 was attributed to the difference in the value of *A*. In other words, the PCT adsorption ability of co-catalyst has a significant effect on the PCT dechlorination. In conclusion, PCT was efficiently dechlorinated and toluene was recovered in a high yield over Pd/C_3N_4 photocatalyst without the use of H_2 under ambient conditions.

Table 1. Dechlorination of PCT to toluene over M/C_3N_4 photocatalysts for 0.5 h and amounts of PCT adsorbed on M in the dark.

M	Pd	Pt	Rh	Au	Ag	-
Toluene / μmol	47	5.7	0.90	0.0	0.0	0.0
Adsorption of PCT on M / μmol	5.1	3.7	2.3	0.0	0.0	-

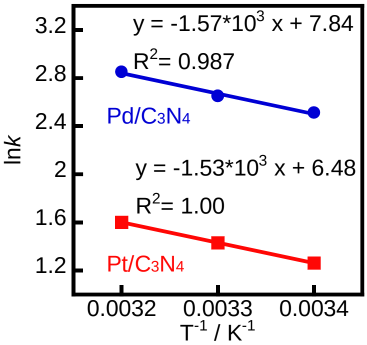

Figure 1. Arrhenius plots for toluene production over Pd/C_3N_4 and Pt/C_3N_4.

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F-7/P-7

Development of Adsorbent/Photocatalyst Hybrids from Co-Digested Sewage Sludge and OFMSW for CO_2 Capture and pollutants air removal.

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As global energy demand continues to rise, particularly in emerging economies, the reliance on fossil fuels remains a significant challenge, with these sources accounting for approximately 50% of Europe's energy mix [1]. In response to the environmental threats posed by anthropogenic CO_2 emissions, the European Parliament has enacted stricter regulations, aiming for net-zero GHG emissions by 2050 [2]. CO_2 not only drives climate change but also contributes to severe public health concerns, with air pollution responsible for around 4.2 million deaths annually, and nearly 90% of the global population living in areas where air quality exceeds WHO limits [3]. Other pollutants, such as volatile organic compounds (VOCs) and nitrogen oxides (NO_x), play a key role in the formation of secondary pollutants like acid rain and photochemical smog, both of which are associated with adverse effects on human health. In response to these challenges, alternative energy sources such as biomass have gained attention, with second-generation biofuels derived from non-edible biomass and waste, such as the organic fraction of municipal solid waste (OFMSW) and sewage sludge (SS), playing a significant role in reducing GHG emissions.

To further mitigate carbon footprints and enhance energy sustainability, CO_2 capture technologies have emerged as essential strategies. Among these, biocarbon materials produced from the pyrolysis of anaerobic codigestion (AcoD) residues of OFMSW and SS— are challenging, since most of the studies found in the literature rely on the use of biomass wastes from agriculture. Biocarbon-based materials may play a key role in pollutant removal, particularly through photocatalytic technology, which has proven effective in eliminating pollutants from both water and air [4]. The combination of adsorbent-photocatalyst hybrids (APHs), particularly those based on carbonaceous materials, enhances pollutant abatement by synergizing adsorption with the photocatalytic oxidation process [5]. These hybrids can also improve photocatalytic stability and efficiency, especially under harsh conditions, by using biochar to store and transfer electrons [6]. Despite these advances, challenges remain in optimizing biochar-based photocatalysts, particularly for gas-phase pollutants such as NH_3, NO_x, and VOCs, with limited research on biocarbon derived from OFMSW and SS. Furthermore, the development of photocatalytic materials responsive to Vis light continues to pose a considerable challenge. Among them, graphitic carbon nitride (g-C_3N_4) has attracted increasing attention due to its favourable properties, including low toxicity, cost-effectiveness, and efficient absorption in the Vis light spectrum [7]. This study focuses on the development of APHs derived from the AcoD of SS and OFMSW to enhance CO_2 capture and photocatalytic pollutant removal particularly for gas-phase VOCs.

Biochemical methane potential tests were initially conducted to evaluate biogas and biomethane production from various SS and OFMSW mixtures at different ratios (75:25, 50:50, and 25:75). The 50:50 ratio demonstrated the highest biogas and biomethane yields, confirming the efficiency of AcoD. Based on these results, a semi-continuous digestion assay was performed in a 5 L reactor over 150 days to assess biomethane production. The resulting digestate was subjected to a pyrolysis process to produce biocarbon, which served as the raw material for the development of APHs. The base material was subjected to thermal, washing, and chemical activation treatments to enhance its CO_2 adsorption capacity. The results showed that these treatments significantly increased the surface area and textural properties of the biocarbon, leading to a notable improvement in CO_2 capture. The APHs were synthesized by incorporating the biocarbon with optimised g-C_3N_4, synthesized via thermal decomposition of melamine, to promote visible-light-driven photocatalysts. A thorough analysis revealed a correlation between the physicochemical properties of the APHs and their depollution performance, demonstrating their potential for VOC treatment. These APHs, prepared via mechanical mixing, exhibited substantial efficiency in CO_2 removal and air pollution control under Vis light irradiation. This approach not only contributes to reducing GHG emissions but also supports the circular economy by transforming waste into valuable resources, such as APH materials, which are highly effective for gas-phase pollutant removal.

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Acknowledgements

"BIOFORAIR" Project, PID2022-138682OB-I00, funded by MCIN/AEI and the European Union.

F-9/P-9

Development of Super-Reductant redox photocatalysts

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Light-driven organic synthesis has greatly advanced with the emergence of photoredox catalysts, which offer significant advantages, including milder reaction conditions. However, most of these developments rely on molecular catalysts or costly transition metals. To address this, we explored the use of semiconductor quantum dots (QDs) as a novel class of redox photocatalysts capable of utilizing visible light. Dabbous et al. [1] and our laboratory studied the photocatalytic capabilities of core CdS, core CdSe, and inverted type I core-shell CdS-CdSe quantum dots (QDs) for carbon-carbon (C-C) bond production through a [3+3]-annulation process, yielding tropane derivatives. Our group discovered that core CdS, core CdSe, and CdS-CdSe QDs were effective catalysts for the annulation reaction over two successive cycles, resulting in the successful synthesis of tropane derivatives [2].

Redox Photocatalysis using QDs systems are generally limited by their reducing potential (typically > −2.0 V vs. SCE). Our goal is to generate an excited state of the anionic or negatively charged species (E_{redox} = −3.4 V vs. SCE) thereby enabling access to a wider range of challenging and energetically demanding organic reactions, which could not be explored before, such as dehalogenation, CO_2 reduction…

Recently, Widness et al. [3] have demonstrated the possibility to excite CdS QDs twice in a process known as ConPET (consecutive photoinduced electron transfer): the first photon generates the anionic form (QD^-), and the second excitation, produces an extremely reducing trion state (QD^{-*}) through Auger processes. This strongly photoreducing catalyst (E_{redox}= −3.4 V vs. SCE) opens up a wide range of unforeseen photoredox opportunities. In addition, Ghosh et al. [4] also showed that an organic catalyst from the perylene diimide (PDI) family can be excited twice, similarly reaching strongly reducing potentials which can be a possible candidate for these reactions.

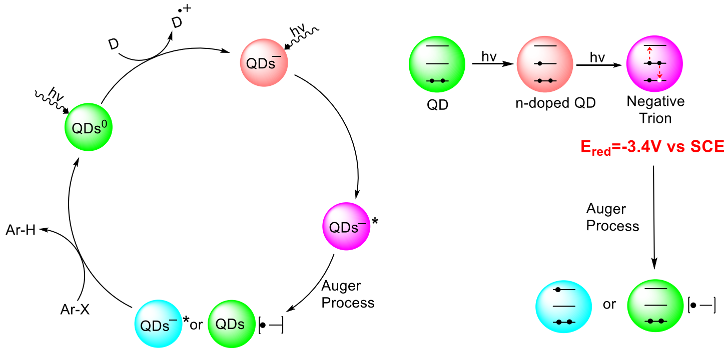

Fig. 1. Proposed photocatalytic dehalogenation using QDs. Adaptedd from reference [3].

In this work, we decided to synthesize different types of QDs and PDIs and explored their efficiency in photoredox dehalogenation reactions (X = I, Br, Cl, and even F). We tested as well greener types of QDs, cadmium-free variants, their possibility to perform ConPET reactions and reach strong reducing potential. We were able to achieve impressive turnover numbers (>10,000 or even >200,000 depending on the QDs). As for PDI, it was applied as well as a photocatalyst reaching comparable TONs to literature [4]. Finally, although both studies [3] and [4] suggest mechanisms based on theoretical assumptions, we conducted detailed EPR and time-resolved studies on our photocatalysts to investigate the formation of anionic or negatively charged species. These analyses aimed to verify the operative mechanism involved in ConPET-driven organic synthesis reactions.

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F-10/P-10

Differences in photocatalytic activity of modified titanium dioxide during the process of carbon dioxide photoreduction

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Poland

Modified titanium dioxide-based samples were obtained via hydrolysis of titanium(IV) isopropoxide using a sol-gel method. In order to establish how different methods of processing the samples impact their activity in the process of carbon dioxide photoreduction, TiO_2 material was modified with nitrates of d-block metals such as zinc, iron(III), and chromium(III). The obtained samples were characterized by scanning electron microscopy (SEM), low-temperature nitrogen adsorption using Brunauer–Emmett–Teller (BET) method, X-ray powder diffraction analysis (XRD), and their photocatalytic activity in the carbon dioxide (CO_2) photoreduction process.

Carbon dioxide photoreduction processes were carried out in a gas-phase system in a glass reactor equipped with a 150 W mercury lamp emitting UV-C light inside a quartz cooler continuously fed with fresh water as described in other works [1,2]. The reactor was filled with gaseous carbon dioxide and 10 mL of liquid ultrapure water in order to allow for the water-splitting reaction and formation of hydrogen in the presence of a photocatalyst.

The composition of the gas phase during the process was analyzed using a gas chromatograph (GC). Comparison of the amounts of products (hydrogen, carbon monoxide, methane, and/or others) obtained in the photocatalytic process of carbon dioxide photoreduction are assumed to be proportional to the photocatalytic activities of various samples. Samples were prepared with the sequential use of microwave-assisted hydrothermal treatment (R) and/or annealing (F). After the modification, samples were rinsed and ground in order to obtain homogeneous photocatalyst powder.

Obtained materials modified with a single d-block metal nitrate and multiple d-block metal nitrates showed varying activity in the carbon dioxide photoreduction process. Most beneficial modifications concerning improving the photocatalytic activity of the samples containing zinc nitrate solution as a main modification agent and/or a blend of multiple salts with zinc nitrate. Obtained samples performed significantly better in the photocatalytic process than the commercially available titanium dioxide (AEROXIDE® TiO_2 P25).

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Acknowledgement

This work was supported by Rector of the West Pomeranian University of Technology in Szczecin for PhD students of the Doctoral School, grant number: ZUT/22/2025 (Grant Rektora 2025 SD doktorant Konrad Sobczuk)

F-11/P-11

Effect of β-FeOOH modification on the photocatalytic and photoelectrocatalytic performance of $BiVO_4$ in the degradation of pharmaceuticals

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The abundant presence of pharmaceutical pollutants in natural waters is nowadays an emerging concern [1]. Although $BiVO_4$ can degrade drug pollutants in both photocatalytic (PC) and photoelectrocatalytic (PEC) processes, its performance is limited by fast electron–hole recombination and low stability, respectively. Therefore, this study aims to investigate how β-FeOOH modification - which may address both issues - influences the PC and PEC performance of $BiVO_4$.

$BiVO_4$ was electrodeposited on SnO_2/F (FTO) substrate as described in [2], then β-FeOOH was deposited by impregnation method [3]. Raman spectroscopy and X-ray diffraction confirmed formation of β-FeOOH phase, while SEM revealed flake-like β-FeOOH nanoparticles (5-70 nm) on the $BiVO_4$ surface. The effect of this modification on the PC and PEC degradation of most abundant pharmaceuticals - paracetamol (PCT), sulfamethoxazole (SMX), and carbamazepine (CBZ) was investigated. In each experiment 6 mL of 20 mg/L solution was irradiated by a 400 nm diode (100 mW/cm^2) in front-illumination mode. In PEC experiment, an external bias of 0.8 V vs. Ag/AgCl (1M KCl) was applied.

Figure 1 shows that β-FeOOH modification of $BiVO_4$ enhances the photocatalytic degradation of PCT and SMX. The results of studies with the probe molecule (terephthalic acid) indicate that more hydroxyl radicals are formed in $BiVO_4$/β-FeOOH systems, and their concentration remains unaffected by deaeration. Thus, unlike bare $BiVO_4$—which generates hydroxyl radicals via superoxide intermediates — $BiVO_4$/β-FeOOH produces them directly from water or hydroxyl ions.

In the PEC process, the modification of $BiVO_4$ with β-FeOOH results in a 1.5- to 2.5-fold increase in the current density and enhanced stability. For bare $BiVO_4$ the current decreases by 55–90%, while it only drops by 12–35% for $BiVO_4$/β-FeOOH. Nevertheless, in photoelectrocatalytic degradation, an opposite effect has been identified. The modification of $BiVO_4$ either reduces degradation efficiency or shows no improvement in performance. Furthermore, energy consumption is either higher or unchanged for $BiVO_4$/β-FeOOH compared to bare $BiVO_4$ (~1.43 kWh/m^3 for PCT, 1.22 and 2.40 kWh/m^3 for SMX, and 1.12 and 1.74 kWh/m^3 for CBZ).

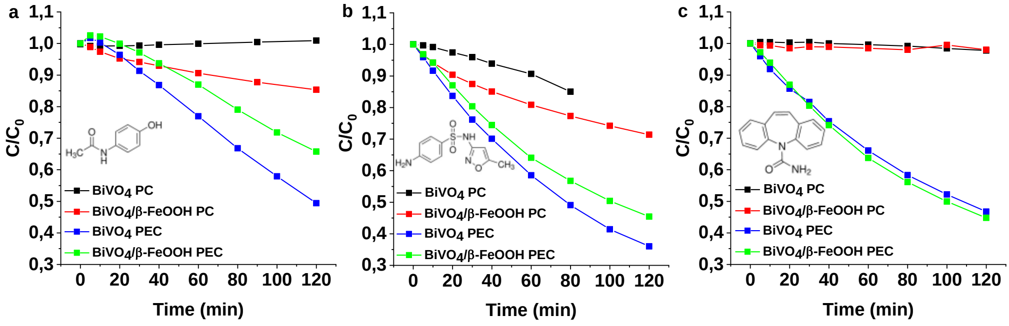

Fig. 1. Influence of β-FeOOH modification on photocatalytic and photoelectrocatalytic degradation of paracetamol (a), sulfamethoxazole (b) and carbamazepine (c).

In summary, the modification of $BiVO_4$ with β-FeOOH leads to different effects on photocatalytic and photoelectrocatalytic processes, improving the performance in former case and reducing in the latter. The reasons for this discrepancy will be discussed.

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F-12/P-12

Engineering perovskite-based electrocatalysts through exsolution and galvanic replacement for sustainable alkaline water electrolysis

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The production of green hydrogen through water electrolysis is viewed as a promising sustainable solution to mitigate climate change and the depletion of conventional fuel sources. In addition, hydrogen is an important feedstock for the chemical industry and its production through electricity will increase the sustainability of several industrial processes for the production of chemicals. Perovskite-based materials are highly efficient functional materials which are deeply studied in various electrochemical applications due to their robust physicochemical properties and flexibility in chemical composition and electronic properties [1]. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is an excellent electrocatalyst for oxygen evolution reaction (OER) in alkaline media and its properties such as high availability of catalytic active sites and fast kinetics distinguish BSCF from other materials in the perovskite family [2].

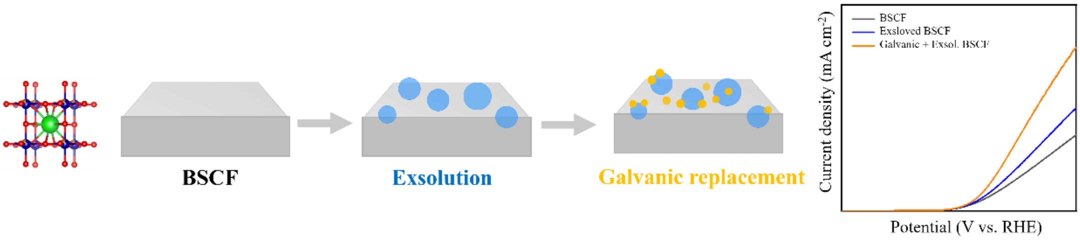

Fig. 1. Engineering BSCF-based materials through combined exsolution and galvanic replacement.

Yet, BSCF contains a significant amount of cobalt (Co), which is accompanied by severe environmental and geopolitical implications. Our main aim is to reduce the Co content, but at the same time improve its OER activity. We achieve this by engineering BSCF through the methods of exsolution and galvanic replacement. The exsolution process introduces multiscale lattice strain in the base material and results in the formation of exsolved nanoparticles, embedded on the surface of the host perovskite, that are more functional and stable [3, 4]. Later, by fine-tuning of the exsolved nanoparticles with low amounts of noble metals through galvanic replacement, we further enhance their OER activity (Figure 1) [4, 5]. These state-of-the-art OER catalysts not only show an increase in their intrinsic catalytic activity, but they do so by a decrease in their Co content. Finally, the practical applicability of our developed and more sustainable BSCF-based catalysts is evaluated in photovoltaic (PV) driven zero-gap alkaline electrolyzers.

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Acknowledgements

This work has received financial support from the European Union HORIZON Research and Innovation Actions under grant agreement ID 101122323 (REFINE).

F-13/P-13

Exploring β-5 lignin model compound photocatalytic conversion on carbon nitride.

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As Net Carbon Zero and the development of the circular economy become critical global environmental issues, developing alternative green energy resources for fossil fuels are an area of significant research activity. Bioenergy is potentially one of the most promising green energy resources due to the large annual global output lignocellulosic biomass originated from forestry and agricultural residues[1]. As a key component of lignocellulosic biomass, lignin, which is comprised of various aromatic monomer units, is a potential feedstock for value added chemical production. The method and mechanism of the cleavage of the linkages between monomers to obtain high value products, however, requires significant investigation as it a complex and non-facile process.

Therefore, this study focuses on the photocatalytic conversion of a lignin model dimer containing the β-5 linkage, which is one of the key components of the lignin structure. In this work it was found that a greater yield of aromatic products was obtained from the photocatalytic conversion of β-5 lignin model compound using carbon nitride (CN) when compared to Evonik P25 titanium dioxide (TiO2). The products of the β-5 model compound photoconversion were determined and C-C bond cleavage was observed by GC-MS. It was also determined that the solvent participated in the reactions due to the introduction of a cyano group to one of the products. Radical quenching experiments revealed that superoxide radicals participated in the CN photocatalytic conversion. The above results reveal for the first time the products and possible mechanism of the photocatalytic transformation of β-5 model compounds using a CN photocatalyst[2].

In future work, a Photoeletrochemical cell will be used and a TiO2/FTO photoanode will be prepared for β-5 lignin conversion and simultaneous hydrogen generation. Hydrogen energy is one of the main pillars of Europe's decarbonization strategy in the coming years, aiming to provide clean solutions for transportation, power generation, and industrial applications[3].

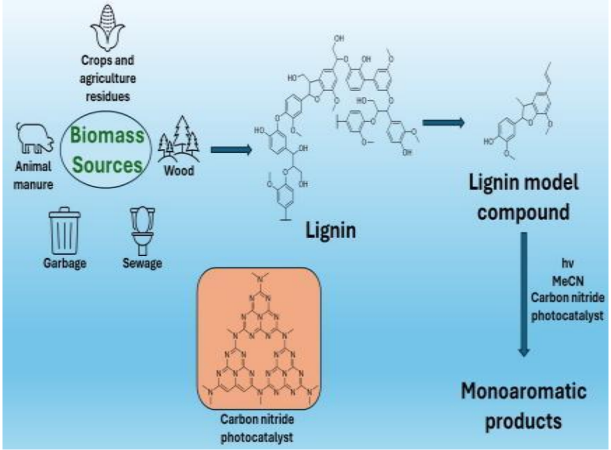

Fig. 1. Schemetic of β-5 photocatalytic lignin conversion. Reproduced with permission[2]. Copyright 2025, Wiley-VCH.

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Acknowledgements

Mr. Junhong Liu gratefully acknowledges financial support from the China Scholarship Council (No.202208440077) for funding his PhD research. We would like to acknowledge the funding provided by the Department of Agriculture, Environment and Rural Affairs for supporting this research (contract number 21/R/475 - ValiD - Valorisation of Digestate using Photocatalysis and Hydrodynamic Cavitation.

F-14/P-14

Ferroelectric-Enhanced Photocatalytic Activity of $BaTiO_3/TiO_2$ Semiconductors for Photooxidation and Hydrogen Production Applications

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Photocatalysis is an efficient and sustainable approach for degrading toxic molecules present in wastewater or for energy applications (e.g., H_2, C1 production). Among the different semiconductors available, titanium dioxide remains the most commonly used semiconductor in photocatalysis due to its abundance, good chemical stability and suitable band edge potentials for H_2 production [1]. However, TiO_2 also presents a very high recombination rate of photogenerated carriers (electron-hole pairs) limiting its intrinsic activity.

One way to enhance the efficiency of photocatalytic materials is to develop assisted-photocatalytic processes. In this respect, charge separation can be driven by the electric field built in the depletion region as a result of the energy discontinuity at the semiconductor/electrolyte interface. Tuning the electronic band structure in the interfacial region is a very effective approach to enhance charge separation efficiency. Ferroelectric polarization is a promising strategy to modify band structures and charge transport performance in heterojunction-based semiconductors. Generating such spontaneous polarization by addition of a ferroelectric material to the photocatalyst provides a strong opportunity to enhance the charge separation [2, 3].

The objective of the present study is therefore to build optimized ferroelectric/TiO_2 semiconductor systems considering $BaTiO_3$ as the ferroelectric material. In order to distinguish between pure heterojunction effects and enhancement due to ferroelectricity, either cubic paraelectric (non-ferroelectric) $BaTiO_3$ or tetragonal ferroelectric $BaTiO_3$ will be considered to obtain $BaTiO_3/TiO_2$ systems. Evaluation of the ferroelectric beneficial effect on the photocatalytic performance will be considered considering both photooxidation reactions or hydrogen evolution reaction.

Barium titanate was obtained through a sol-gel process using titanium butoxide and $Ba(OH)_2$ as precursors followed by a hydrothermal step at 200°C for 24 h. The resulting material was then washed with acetic acid, water and ethanol before being dried at 80°C for 12 h. Formation of $BaTiO_3/TiO_2$ systems was obtained through the addition of Ti butoxide to various $BaTiO_3$ samples followed by calcination at 500°C for 2 h. The final relative $BaTiO_3/TiO_2$ molar ratio was varied from 1/0.125 to 1/3.

First experiments were performed in order to selectively obtain either cubic paraelectric $BaTiO_3$ or tetragonal ferroelectric $BaTiO_3$ without modifying size or shape. In this respect, the addition of ethanol to the sol-gel synthesis during the preparation of barium titanate selectively controls the exclusive formation of the ferroelectric phase. Removing ethanol on the opposite leads to the formation of a pure cubic phase as confirmed by XRD and Raman spectroscopy. Moreover, increasing the temperature used for the hydrothermal step also allows to favor the formation of a ferroelectric $BaTiO_3$ phase. Finally, since the $BaTiO_3$ ferroelectric phase is expected to be thermodynamically metastable, control experiments were also performed to verify that the final calcination treatment used during the $BaTiO_3/TiO_2$ preparation does not influence the final proportion of ferroelectric phase obtained.

$BaTiO_3/TiO_2$ photocatalytic systems were then synthesized using both ferroelectric or non-ferroelectric $BaTiO_3$ substrates considering various proportions of TiO_2 deposited onto $BaTiO_3$. Attention was paid to avoid any carbon contamination coming from the sol-gel approach and potentially biasing photocatalytic activity evaluation. Results indicate that at iso-amount of TiO_2 used, employing a ferroelectric $BaTiO_3$ substrate leads to a strong increase of the activity by 80% for the photocatalytic degradation of formic acid. Optimization of the ferroelectric effect will also be presented through determination of the optimized amount of TiO_2 to be added and description of the characteristics of the $BaTiO_3/TiO_2$ interface by TEM analysis. Finally, after addition of Cu metallic NPs onto the various $BaTiO_3/TiO_2$ systems, the beneficial effect resulting from ferroelectricity will also be evaluated for the hydrogen evolution reaction.

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Acknowledgements

All authors thank ANR for its financial support (ANR-22-CE05-0006).

F-15/P-15

Impact of Pt impregnation on P25 for visible light photocatalytic applications

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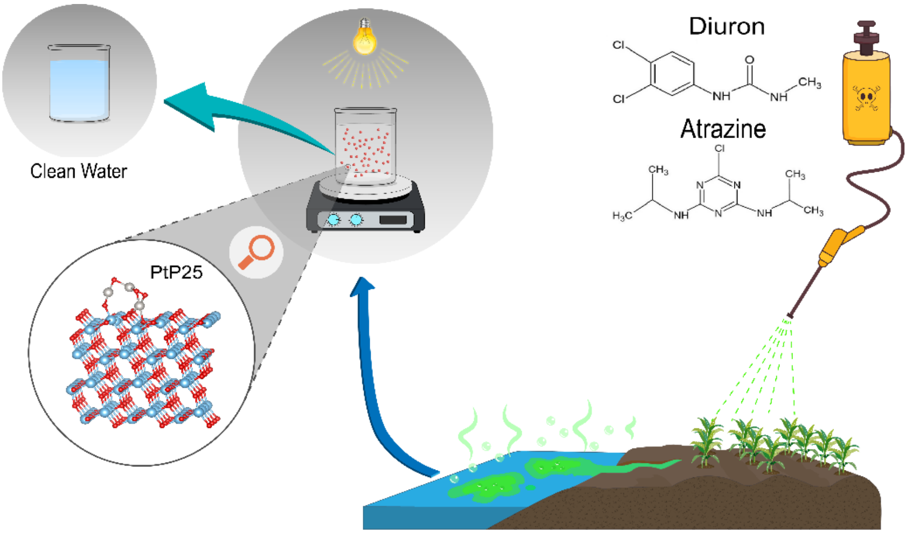
The detection of herbicides like diuron (DIU) and atrazine (ATZ) in water bodies is concerning scientists related to their environmental and health risks [1]. The potential risks are rising, since current water treatment techniques are not effective with these kinds of pollutants. Photocatalysis is a promising method that can be used for water treatment [2,3]. Titanium dioxide (TiO_2) is a photocatalyst with good performance under UV range, and its commercial form is commonly known as P25 that is a combination of 80 % anatase and 20 % rutile phase. However, to use the solar spectrum better, it is necessary to have photocatalysts that are active under visible range, as in solar spectrum 42 % is visible light and only 5% is UV. In this case we doped P25 with Pt nanoparticles to reach better light absorption, and to analyze the interaction of their atoms and evaluate their photocatalytic activity for degradation of herbicides. P25 was impregnated with different percentages of Pt (0.2%, 0.5% and 1%). XRD showed that Pt with 1% loading contains Pt_3O_4 and most probably the Pt particles are also entering in the P25 lattice. For all the samples it was possible to identify a band gap and Valence band that correspond with TiO_2 and PtO_x, supporting a heterojunction behavior. Photocatalytic activity was evaluated under visible light using white LED light. The best photocatalytic DIU removal was observed for the sample impregnated with 0.2%PtP25 reaching ~20% degradation in comparison with ~7 % removal of the P25 in 5 h irradiation time. While for ATZ degradation during 5 h irradiation 0.2%PtP25 sample made ~7% degradation in comparison with ~1% removal of the P25. Based on experiments, the photocatalysts are stable and can be reused. Pt impregnation on P25 creates a heterojunction structure that improves their photocatalytic performance under visible light making these photocatalysts useful for water treatment applications.

Fig. 1. Graphical abstract.



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Acknowledgements

Nanomo and ECE units, university of Oulu. NANOCAT project from Kvantum institute of University of Oulu. Grant 20240014 from Oulun Läänin Talousseuran Maataloussäätiö. Grant 2024008 Vesitekniikan tutkimus.

Impact of temperature on the efficiency and stability of a TiO_2-based photoelectrochemical cell for solar hydrogen production

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Solar fuels and, in particular, hydrogen production through solar water splitting using a photoelectrochemical (PEC) cell, are considered one of the most promising ways for storing large quantities of solar energy over long periods of time [1]. The high cost and low efficiency of PEC systems are the two main obstacles to their development [2]. As the key component of a PEC cell, research has focused on the manufacture of high-performance, stable and scalable photoelectrodes. However, at present, no single material meets all these requirements [3]. Thank to doping, co-catalyst, surface and morphology control, photoelectrodes based on metal oxides nearly reached their theoretical conversion efficiency limits [4]. This has led to a shift in research focus toward studying the complete PEC system, scaling it up, and assessing its performance under real operating conditions [5].

Like all other solar and electrochemical systems, PEC cells are highly sensitive to operating conditions such as temperature. To ensure optimal performance and longevity, PEC devices must operate within a controlled temperature range. Additionally, for effective scale-up, the cell configuration and design have to be sufficiently studied and optimised [6]. Recently, metal oxides photoanodes such as Si-doped $\mathrm{Fe_2O_3}$, $\mathrm{WO_3}$, $\mathrm{BiVO_4}$, $\mathrm{CuWO_3}$ and $\mathrm{TiO_2}$ have been investigated to assess the impact of temperature on photocatalytic performance. Within the studied temperature range, typically between 25°C and 65°C, these semiconductor photoanodes exhibit a positive correlation between photocurrent density and temperature [7–11]. Some recent studies [11,12] have shown that the efficiency of $\mathrm{TiO_2}$ photoanodes on FTO is improved with increasing temperature, between 20°C and 50°C, and even more so at low anodic potentials [13]. Understanding the effects of temperature on PEC cells is crucial for both fundamental research and practical applications. Temperature influences key processes such as charge carrier dynamics, recombination rates, reaction kinetics, and mass transport, all of which directly affect overall efficiency. Furthermore, long-term stability and material degradation under varying thermal conditions remain critical challenges for PEC deployment.

In this study, our main objective is to measure $\mathrm{TiO_2}$ based PEC cell efficiency between 20 and 80°C. Secondly, we aim to quantify the effects of temperature on key parameters, including photoanode optical absorption, recombination rate, kinetics and onset potentials of the hydrogen and oxygen evolution reaction (HER/OER) and electrolyte resistance. Lastly, we will assess the stability and durability over extended operation. To achieve these objectives, we will employ characterisation techniques such as UV-Vis spectroscopy, linear sweep voltammetry, chronoamperometry and photoelectrochemical impedance spectroscopy. Additionally, we will develop an equivalent electrical circuit model to represent the system components, including the photoanode substrate and photo-catalyst, electrolyte and cathode. The model enables the evaluation of the temperature-dependant behaviour of each individual component. This experimental study aim to provide a deeper understanding of how temperature influence the efficiency, stability and fundamental processes within a PEC cell, contributing to the optimisation of PEC devices for practical solar hydrogen production.

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F-17/P-17

Influence of Metal Ratios and Support Materials on the Photo-Fenton Activity of Cu-Fe Bimetallic Catalysts

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Advanced oxidation processes (AOPs) are very successful technologies that use highly reactive oxygen species, primarily hydroxyl radicals (•OH), to break down organic contaminants in water and provide a sustainable solution to environmental issues. Among them, the photo-Fenton process stands out due to its unique ability to generate highly reactive hydroxyl radicals that enable the rapid and efficient degradation of a wide range of pollutants. The stability and activity of photo-Fenton catalysts can be enhanced by adopting strategies like metal doping, and support modification, making them more suitable for sustainable applications in wastewater treatment.

In this study, we synthesized a series of bimetallic Cu-Fe photo-Fenton catalysts by varying the Cu/Fe metal ratios on silica and alumina supports to investigate the role of metal ratios and support materials on the structure and activity of the catalysts. Fe was incorporated into the supports at a molar ratio of 0.005 (Fe/Al or Fe/Si), while Cu was loaded at varying molar ratios of 0.005, 0.01, and 0.02 (Cu/Al or Cu/Si). Silica-based Cu-Fe catalysts were prepared by direct synthesis followed by calcination, while alumina-based Cu-Fe catalysts were prepared from an ammonium dawsonite precursor followed by wet impregnation and calcination. To investigate how the metal ratios and supports influence the properties of the catalysts, such as phase formation, porosity, elemental distribution, and electronic properties, a comprehensive characterization of the catalysts was carried out using the following techniques: X-ray diffraction (XRD), N_2 physisorption, scanning electron microscopy (SEM) with elemental analysis (EDAX), transmission electron microscopy (TEM), UV-Vis diffuse reflectance spectroscopy (DRS), solid-state photoluminescence (PL), time-correlated single photon counting (TCSPC) and electron paramagnetic resonance spectroscopy (EPR). The photo-Fenton catalytic activity of the samples was investigated in a batch slurry reactor using coumarin as a probe for detecting hydroxyl radicals.

XRD analysis confirmed the amorphous nature of silica with distinct CuO peaks, whose intensity increased with Cu loading for silica-supported catalysts. In contrast, alumina-supported catalysts showed only γ-Al_2O_3 phases with no visible metal oxide peaks of Cu and Fe, indicating high dispersion and strong interaction between the metal species and the support. The presence of Fe^{3+} and Cu^{2+} was confirmed in both supported catalysts using EPR spectroscopy. Catalysts supported on alumina showed more refined hyperfine splitting, indicating higher metal-support interactions. TEM analysis revealed homogenous metal distribution in most samples, with the exception of CuO aggregation in high Cu-loaded silica catalysts, illustrating the effect of metal loading in dispersion. Based on DRS spectra, both supported catalysts showed absorption in the visible region due to Cu clusters and charge transfer transitions. Surface defect-related emissions were identified from PL spectra, and TCSPC tests showed that the catalysts had short lifetimes that should be optimized for improved photo-Fenton efficiency. Cu-Fe catalysts on alumina support showed higher activity than those on silica support due to better metal dispersion, stability, and efficient charge transfer dynamics, with the optimal Cu concentration promoting coumarin degradation. It was shown that the generation of hydroxyl radicals by H_2O_2 activation, either in the dark or under visible light, strongly depends on the interactions between copper and iron-containing phases. The results show that the photo-Fenton activity of multicomponent catalysts can be enhanced by varying metal ratios and support materials.

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Insights into the Coordination Effect on Copper Restructuring in Post-Metalated MOFs During Photocatalysis

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Metal-organic framework (MOF)-based photocatalysts can be tuned through various structural modifications for enhancing their photocatalytic performance. Very recently, we figured out that Cu^{2+} embedded in UiO-66-$(COO)_2$ (called UiO-66-$(COOH)_2$-Cu) undergo an *in-situ* restructuring during photocatalytic formic acid (FAc) dehydrogenation under simulated solar-light.[1] Herein, multivariate (MTV) UiO-66 derivatives with varied linker ratios (BDC:BTCA) represented as (x:y) were synthesized (fig.1A) and post-metalated with Cu to assess the impact of these functionalities on Cu coordination and its *in-situ* restructuring. The reaction mechanism was investigated using complementary *operando* techniques, including Fourier Transform Infrared spectroscopy (FTIR) and X-ray absorption spectroscopy (XAS), which allow monitoring the chemical structure evolution of UiO-66(COOH)x-Cu, as well as changes in Cu oxidation states during the reaction. Results showed that the activity increases with the increase of BTCA concentration (fig.1B). Also, a concurrent formation of anhydride between two free carboxylate groups was observed on the surface (fig.1C). The evolution of this anhydride showed an increase with the rise of BTCA ratio (fig.1D). Then a linear correlation between the sample activity and the amount of anhydride (fig.1E) was demonstrated. Furthermore, XAS reveals that the Cu^{2+} species initially coordinated to the free carboxylate groups undergo *in-situ* restructuring to Cu^{+} and Cu^{0} under solar-simulated light in the presence of FAc (Fig.1F). DFT calculations highlight the influence of free carboxylate groups spatial arrangement on Cu coordination stability, thereby affecting the rate and yield of the restructuring process. This comprehensive study underscores the significance of metal coordination in influencing the photocatalytic activity, paving the way for novel photochemical approaches to nanosynthesis of metal clusters in MOFs.

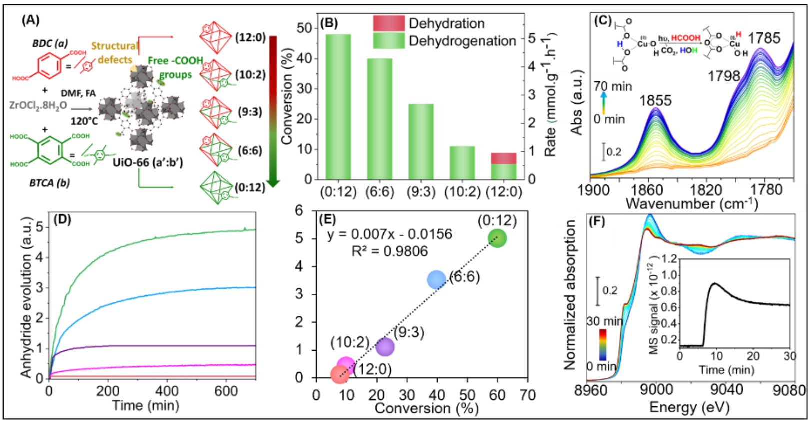

Figure 1. (A) Schematic illustration of MTV-UiO-66 derivatives, (B) Photocatalytic performance of different samples in FAc reforming, (C) IR spectra (1900 – 1700 cm^{-1}) of (0:12) sample and (D) Anhydride band area evolution vs. time of the various samples, (E) Correlation of steady-state anhydride band area with the activity, and (F) Time-resolved Cu-XANES and H_2 evolution (inset) during FAc dehydrogenation under visible light ($\lambda \geq 390$ nm).

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Acknowledgements

The authors acknowledge MOFtoH2 (ANR-21-CE50-0022-01), MOF2H2 project funded by the European Union (101084131), Label d'Excellence (SunToChem), ANR-10-EQPX-45, ANR-HYPH2, and DIM MaTeRE (MOFPlasma Project) for the financial support.

F-19/P-19

IR characterisation of powder and membrane-based metal oxide catalysts for photothermal CO_2 reduction

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The increase in the average concentration of greenhouse gases (GHGs) observed over the last 50 years makes it urgent to find new ways to reduce the level of CO_2 in the atmosphere.[1] Among the possible strategies, Carbon Capture and Utilization (CCU) began to attract increasing attention because of its involvement not only in the permanent storage of the captured CO_2, but also in its utilization and conversion into new sources and products, such as chemicals or renewable fuels.[2]

In this respect, photocatalytic CO_2 reduction represents a more sustainable alternative to conventional thermo-catalytic approaches.[3]

A possible application of this approach is the one suggested in the EIC-Pathfinder project DAM4CO2,[4] which aims to capture and convert CO_2 into C_4-C_9 renewable fuels through the synergetic integration of two reactions in cascade (Reverse Water Gas Shift and Fischer-Tropsch) over catalysts embedded in Mixed Matrix Membranes (MMMs). As a project requirement, no critical raw materials according to EU regulation should be used in the catalyst formulation, leading to the design of innovative materials featuring only Earth-abundant and low supply risk elements.

In this perspective, different catalysts based on metal oxides of earth-abundant elements (such as Fe, Ni and/or Cu) were synthesised and tested under photothermal conditions (200-250 °C, atmospheric pressure, under sun-like irradiation). The catalysts in powder form were firstly characterised by coupling basic characterisation (such as X-ray diffraction and volumetry) with *in situ* IR spectroscopy (Figure 1) to study the nature of the interactions occurring between the reagent/products and the catalyst surface. Various MMMs combining different catalysts-polymeric matrices were then prepared, tested and characterised to investigate the properties of the composite materials.

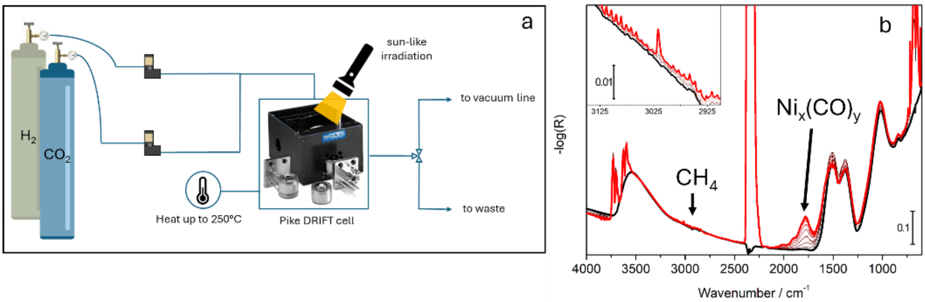

Figure 1. Schematic representation of the set-up used during the *in-situ* IR measurement (a) and IR spectra of commercial Ni-NiO catalyst under 1:1 CO_2:H_2 feed at 200 °C and sun-like irradiation (b).

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Mayenite Electride-Based Photo-Thermal Catalysts for CO_2-to-Methane Conversion

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A sustainable method for the production of renewable solar fuels is the photothermal catalytic conversion of carbon dioxide (CO_2) to methane (CH_4). In this study, we report the development and testing of a composite catalyst for the photothermal methanation of CO_2 under mild conditions. The catalyst consists of a heterostructure composed of mayenite electride (C12A7: e^-) and TiO_2 modified with metal nanoparticles (Fe, Co, and Ru) by surface deposition. Mayenite electride (Figure 1) is selected because of its good electrical conductivity and electron-donating capacity. TiO_2 was used as a support material to assist with photogenerated charge separation, improve catalyst dispersion, and keep its structural stability [1–3], while transition metals are introduced to provide active sites for CO_2 activation and hydrogenation.

Catalytic performance was formed in a continuous flow gas phase reactor using CO_2 and H_2O as reactants under UV illumination and moderate thermal input (≤ 200 °C). The metal-deposited catalyst showed significantly higher CH_4 production rates compared to the unmodified mayenite electride and mono-metallic systems, evidencing a synergistic effect among the co-deposited metals. Structural and morphological characterization (XRD, SEM-EDX) confirmed the retention of the mayenite crystal phase and a uniform metal dispersion on the surface. Thermogravimetric analysis (TGA) demonstrated the thermal stability of the mayenite electride under the photothermal operating conditions used in this study. The preparation of mayenite electride-TiO_2 composites modified with metal nanoparticles led to higher surface areas and extended light absorption, which enhanced catalytic performance.

This research showcases the potential of surface-modified mayenite electrides as efficient photothermal catalysts for CO_2 methanation. Further studies are underway to improve understanding of the fundamental reaction mechanisms by looking at the material's light-related electronic properties and surface spectroscopic analyses, highlighting the distinct contributions of each metal component to methane formation.

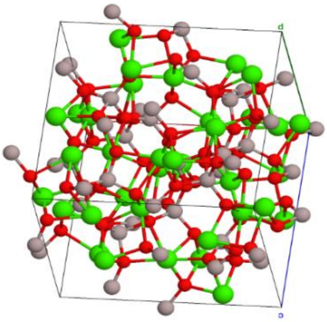

Fig. 1. Crystal structure of mayenite electride ($Ca_{12}Al_{14}O_{33}$: e^-).

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This work has received financial support from the FPI-María de Maeztu PhD Grant funded by MCIN/AEI and FSE under grant agreement No PRE2021-098716.

F-21/P-21

Metal Ion Effects and Structure Modification Influence on the H_2O_2 Production Efficiency of Templated Poly(Heptazine Imides)

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Polymeric carbon nitride (PCN) is in an attractive and unique organic polymer. This low-cost heptazine-based polymeric semiconductor exhibiting outstanding stability and ability to efficiently drive photocatalytic oxidation and reduction reactions under light irradiation represents one of the best candidates for photocatalyst for solar-fuels production. A particularly interesting class of PCN is represented by ionic PCN, also known as poly(heptazine imide) (PHI). Following recent research in our group on this material class [1-3], we have investigated various approaches to improve the efficiency of PHIs in hydrogen peroxide production (H_2O_2). H_2O_2 is a versatile chemical with manifold applications in disinfection, chemical synthesis, or textile industry.

In our studies, we show the capability of PHIs, synthesized using a hard template method utilizing different mesoporous silica-based materials (SBA-15) and SiO_2 spheres, to oxidise alcohols, producing the corresponding aldehyde and simultaneously H_2O_2. By introduction of alkali and transition metals, we were able to enhance the structural understanding of the resulting PHIs and tune their reactivity. With the insights acquired from these studies, future photocatalytic material designs are greatly enhanced [4, 5].

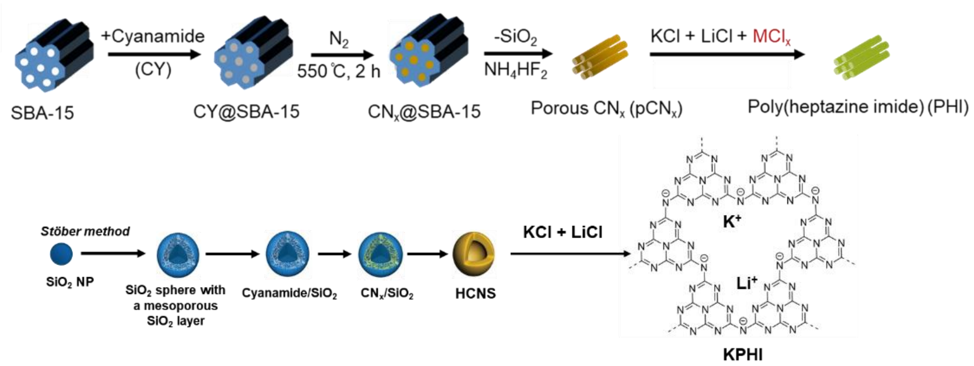

Fig. 1. Synthesis routes for new ionic carbon nitrides (PHIs).

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Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Projektnummer 364549901 – TRR 234 [Projects B6, B10].

F-22/P-22

Optimisation of bi-metallic Pt-Cu/TiO_2 for gas phase CO_2 photoreduction for the production of solar fuels

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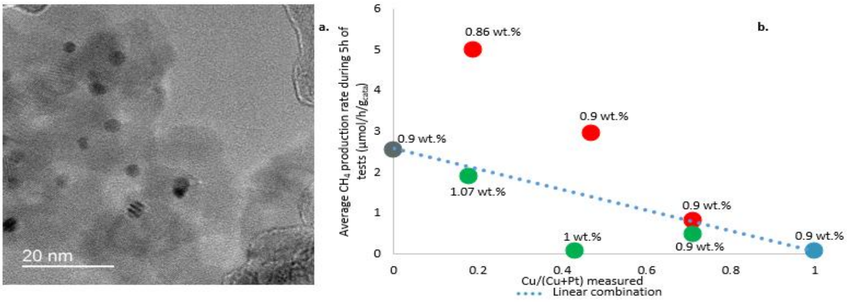
The excessive concentration of CO_2 in the atmosphere is an alarming environmental challenge, contributing to the climate change and the rise of the oceans [1]. Photocatalytic CO_2 reduction driven by solar light appears as a potential contribution of synthesizing solar fuels by using CO_2 [2]. Nevertheless, until now, the efficiency remains still low, hindering large scale applications. It is admitted that plasmonic nanoparticles can direct reactions towards specific routes, and raise both reaction rate and selectivity towards some products [3].

Experimentally, bi-metallic plasmonic photocatalysts (NP size= 3 nm (Fig. 1. a.)) were synthesized by depositing bimetallic copper and platinum nanoparticles on titanium dioxide (anatase, absorbing in the UV region with a band gap of 3.2 ev) [4]. Two synthesis techniques have been attempted, aiming at 1wt.% of total (Cu+Pt) metal loading and varying Cu/Pt ratio: (i) chemical co-reduction of both metal precursors: $H_2PtCl_6.xH_2O$, $Cu(NO_3)_2.xH_2O$, or (ii) chemical sequential reduction of the Pt salt followed by the Cu salt in an aqueous dispersion of the support. The UV-VIS study, reveals from the absorption around 600 nm that Cu species (resulting from the co-reduced route) are essentially CuO_x, however the CuO_x is a minority phase for the other synthesis route. Under visible light illumination (λ> 400 nm) and a CO_2/H_2O (98/2) flow mixture, methane is produced with 100% selectivity, regardless of the synthesis route and the composition of the bimetallic photocatalyst. The study of the surface composition of the materials by XPS shows that platinum is present mainly in its metallic form Pt^0. But for copper it is difficult to differentiate between Cu^0 and $Cu^{(+I)}$. For the co-reduction synthesis route, the quantity of Cu at the surface and in the bulk are almost similar regardless of the composition of the bimetallic, but for sequential reduction the surface is enriched with Cu for the photocatalysts with low nominal content of Cu. Thus, it can be an explanation for the higher quantity of CH_4 produced for the co-reduction compared with sequential reduction. The general trend, by increasing Cu/(Cu+Pt) nominal content, is a decrease in the visible photocatalytic activity, probably due to the diminution of the intraband transitions of Pt with the lower amount of Pt. A synergistic effect is observed for the $Cu_{0.2}Pt_{0.8}/TiO_2$ composition, which exhibits a significantly higher average CH_4 production rate compared to the weighted average productions observed over the monometallic references (Fig. 1. b.).

In conclusion, the photocatalytic activity can be enhanced by tuning and finding an optimum $CuO_x/Cu^0/Pt$ ratio. The different resulting material have been characterized by means of bulk, surface, structural and optical characterizations. Structure/activity correlations will be presented.



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Acknowledgements

This work has benefited from French State aid managed by the Agence Nationale de la Recherche under France 2030 plan (ANR-22-PESP-0010 Projet ciblé "POWERCO2") within the SPLEEN PEPR.

Optimising WO_3/TiO_2 heterojunctions: A systematic approach for enhanced performance un photocatalytic/photoelectrocatalytic remediation applications.

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Introduction.

Rapid global population growth exacerbates water and air pollution issues, leading to the proliferation of disease-carrying airborne microbes, and harmful pollutants like nitrogen oxides (NOx). The eradication of these pollutants is crucial for maintaining public health. Recent studies in photocatalysis have been directed towards developing environmentally friendly solutions, such as nanocomposite photocatalysts, which offer high surface and improve efficiency. In this work, we present the design and synthesis of nanostructured WO_3/TiO_2 heterojunction film coatings to produce layered photocatalytic systems able to eliminate contaminants from the environment.

Materials and Methods

Photocatalysts were grown on borosilicate and ITO glass substrates using chemical vapour deposition (CVD) methods. N_2 gas was used as the carrier gas and introduced to the reactor through a baffle manifold to ensure laminar flow.

CVD synthesis of WO_3: WO_3 photocatalysts were synthesised through aerosol-assisted chemical vapour deposition (AAVDC) using a precursor solution, composed of tungsten hexacarbonyl (W(CO)6) dissolved in a 2:1 mixture of acetone and methanol. This solution was aerosolised using an ultrasonic humidifier and transported into the reactor at a flow rate of 4 L min^{-1}. The reactions were conducted at a temperature of 355°C.

CVD synthesis of TiO_2: TiO_2, photocatalysts were synthesised via atmospheric-pressure chemical vapour deposition (APCVD). Titanium tetra-isopropoxide (TTIP) was heated to 120°C, achieving a vapour pressure of approximately 52 torr. The vapours were directed into the reactor at a flow rate of 3 L min^{-1}, and reactions occurred at 450°C. Various TiO_2 film coatings were produced with specific reaction times: 30 seconds, 1, 2 y 4 minutes.

CVD synthesis of WO_3/TiO_2 heterojunctions: TiO_2 heterojunctions were fabricated on the different glass substrates through the sequential chemical vapour deposition (CVD) of WO_3 and TiO_2, as detailed earlier.

Results and discussion.

Nanostructured WO_3/TiO_2 heterojunction systems, have been nanoengineered and synthesized to enhance their surface and photogenerated charge carrier separation. The uniqueness of this research work relies on the coordinated approach to improve material´s design and synthesis by growing nanostructured WO3/TiO2 heterojunctions onto different glass substrates (silica-coated and ITO glass substrates) to generate highly active photocatalytic materials (Figure 1). Interestingly, the nanostructured WO_3/TiO_2 heterojunction presented in this work showed unprecedent photocatalytic activity for a thin film coating in the degradation of a model organic pollutant (stearic acid). Such approach can potentially represent a major breakthrough in the design of highly active photocatalytic systems, by maximizing their surface area without altering the homogeneous light irradiation and photonic efficiency within the photoreactor, enhancing the photocatalytic process.

In summary, the nanostructured WO_3/TiO_2 heterojunction film coatings will undergo assessment for their effectiveness in photocatalytic and photoelectrocatalytic remediation applications. This evaluation aims to eliminate various contaminants, including bacteria, viruses, and NOx.

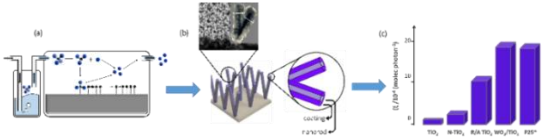

Fig. 1. a) Bottom. Scheme of the synthesis of nanostructured WO_3/TiO_2 heterojunction coatings. Top: SEM and TEM images of WO_3/TiO_2 heterojunction coatings. c) Photocatalytic activities (ξ, molecules degraded per incident photon, molecule x photon^{-1}) of different flat and heterojunction coatings. Typical ξ values of a P25 Evonik dip-coated film (5 wt% dispersion) is included for reference.

Acknowledgements

Authors acknowledge the financial support of the Spanish Ministry of Science and Innovation and the Spanish State Research Agency (MCIN/AEI/10.13039/501100011033) through the project POLLUTWIN (TED2021-129162B-C21) and the European Union (NextGenerationEU/PRTR). C. S-V acknowledges Comunidad de Madrid for financial support through the Programa de Atracción de Talento “César Nombela” 2023 (2023-T1/ECO-29048).

F-24/P-24

Oxygen Vacancy Engineering in Nano-CeO_2 for Long-Term Photocatalytic Removal of VOCs

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The removal of volatile organic compounds (VOCs) is essential for improving indoor air quality. Cerium dioxide (CeO_2) has attracted considerable attention due to its redox-active surface and its ability to generate reactive oxygen species under UV irradiation. However, the complete mineralization of toluene remains challenging. The aromatic ring-opening step requires high activation energy. It often leads accumulation of partially oxidized intermediates and causes to photocatalytic deactivation.

In this study, we utilize metal-organic frameworks (MOFs) as precursors to engineer oxygen vacancies in nano-sized CeO_2. MOFs enable precise control over the formation of oxygen vacancies during thermal decomposition through their porous structures and highly organized metal-ligand frameworks. These vacancies play a key role in enhancing catalytic activity by providing active sites for oxygen molecule activation and increasing the generation of reactive species. The defect-engineered CeO_2 exhibited significantly enhanced photocatalytic activity and long-term stability in gaseous toluene degradation. It maintained stable performance during repeated cyclic tests under high toluene concentrations and it effectively decomposed toluene with removal efficiency of approximately 80% for 24 hours in a continuous gas flow system. Notably, its high photocatalytic activity was sustained even under 5% of ambient O_2 concentration. This behavior is ascribed to the presence of abundant bulk oxygen vacancies, which act as internal oxygen reservoirs and alleviate surface oxygen depletion during extended photocatalytic operation. Position resolved EELS analysis revealed elevated Ce^{3+} concentrations not only at the surface but also within the bulk lattice indicating the formation of deep-seated oxygen vacancy sites. Furthermore, surface and bulk oxygen vacancies facilitate reactive species generation and charge separation supporting stable toluene mineralization even in oxygen-deficient conditions are confirmed with EPR and PL analysis. These results highlight the potential of oxygen vacancy controlled CeO_2 as a robust photocatalyst for practical air purification systems. Its high durability and performance under low-oxygen conditions make it a promising candidate for VOCs removal in real indoor environments.

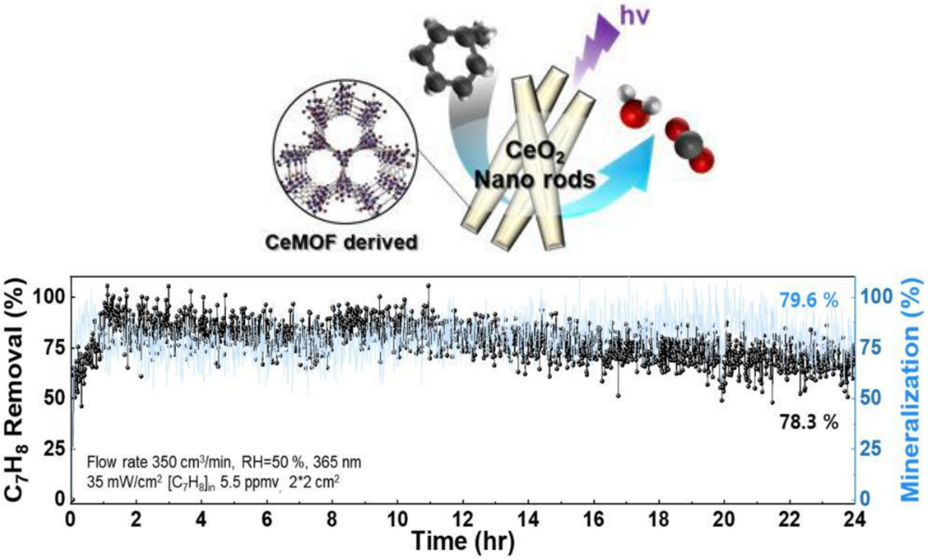

Fig. 1. Long-term performance for toluene degradation.

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Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. NRF-2021R1A5A1084921).

F-25/P-25

Photocatalysis meets exsolution: case study of Cu-based HER co-catalysts

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In semiconductor photocatalysis for water splitting, one important factor is to promote efficient charge separation within the catalyst after photoexcitation. This can be achieved by adding a nanoparticle co-catalyst on the surface of the semiconductor, which extracts the photogenerated electrons/holes while also providing a suitable catalytic site for the desired reaction, it being hydrogen evolution reaction (HER) or water oxidation [1].

Over the last decades, a new method of forming nanoparticles supported on metal oxide materials has emerged: redox exsolution. Rather than depositing the co-catalyst directly onto the surface from a solution or the gas phase, its elements are embedded in the oxide lattice (usually a perovskite) through doping. With thermal treatment, usually under reducing conditions, oxygen vacancies are created at the surface, which leads to the diffusion and reduction of the most easily reducible metal in the lattice (in this case the desired co-catalyst material) and the formation of nanoparticles on the surface [2]. Compared to pre-deposited co-catalyst nanoparticles, exsolved nanoparticles are socketed into the lattice, leading to a strong metal-oxide interaction and making the particles more resistant to agglomeration. In addition, the metal can be re-absorbed into the host lattice under oxidising conditions and exsolved again later. This unique property would allow to regenerate the co-catalyst, further enhancing the lifetime of the material. Because of these properties, exsolution is quickly gaining interest as a method to prepare oxide-supported nanoparticles for catalysis [3, 4].

In this work, we apply the idea of exsolution to generate a dynamic photocatalyst/co-catalyst couple based on Cu-doped $SrTiO_3$ (STO) and Cu-doped $SrTi_xFe_{1-x}O_3$ (STF). Both perovskite matrices are first produced, whereas the particle size and composition of the mixed oxides are tuned systematically. We trigger exsolution of Cu by standard reductive conditions, but also investigate the possibility to exsolve Cu via photoreduction. We show the ability of exsolved Cu/STO and Cu/STF to catalyst HER under UV and visible light and compare their performance with benchmark Cu/STO and Cu/STF photosystems prepared using conventional methods such as photodeposition.

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Acknowledgements

The research is funded by the Austrian science fund (FWF) [10.55776/COE5](Cluster of Excellence MECS)

F-26/P-26

Photocatalytic inactivation pathways of *E. coli* bacteria using bismuth oxyiodide photocatalysts

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Water contamination by pathogenic microorganisms is a growing global concern. Advanced Oxidation Processes (AOPs) are widely studied for water disinfection, with TiO_2 P25 showing good photocatalytic performance under UV light [1]. However, its UV dependence limits practical use, highlighting the need for materials that can work under visible irradiation [2]. This study investigates the photocatalytic inactivation of *Escherichia coli* (*E. coli*) using bismuth oxyiodide ($Bi_xO_yI_z$) photocatalysts synthesized through a low-energy consuming pH-dependent co-precipitation method [3]. The performance of $Bi_xO_yI_z$ was compared to the well-established TiO_2 P25 benchmark. Inactivation assays were conducted in aqueous solutions at neutral pH. Notably, $Bi_4I_2O_5$-co exhibited exceptional antibacterial properties, achieving over 99% bacterial inactivation within just 10 minutes of irradiation under visible light (White LED), demonstrating its remarkable efficacy. Since no ROS formation was detected by the bismuth oxyiodide photocatalysts through DMPO spin-trap EPR experiments, a non-ROS-mediated photocatalytic bacterial inactivation mechanism is proposed. This mechanism suggests a direct process where photogenerated electrons and holes [4], together with bismuth ions in solution, interact with and disrupt bacterial cellular components

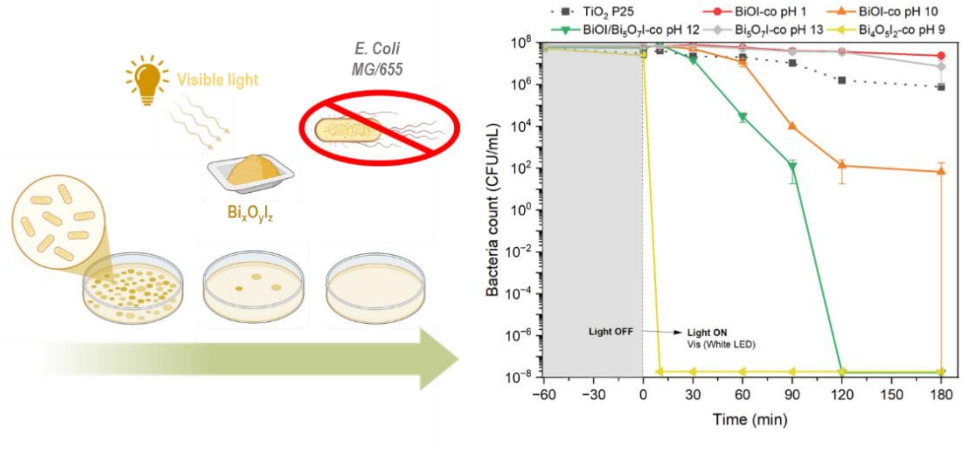

Fig. 1. *E. coli* inactivation under visible light using bismuth oxyiodide ($Bi_xO_yI_z$) photocatalysts.

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The funding for this work was provided by the projects PID2022-141812OB-I00 from the AIE (Spanish Research Agency) and ILINK22054 from CSIC. We would also want to thank the Ministry of Universities (Spain) for its financial support through the FPU22/01793 predoctoral scholarship to Andrea Martínez-Topete.

K-HEALTHinAIR Project: Annual Monitoring of Air Quality in Hospital Environments and Its Impact on Health

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Indoor air quality (IAQ) in healthcare facilities plays a pivotal role in ensuring patient safety, protecting the health of medical staff, and maintaining overall environmental quality. One of the most critical aspects affecting IAQ in hospitals is the performance of heating, ventilation, and air conditioning (HVAC) systems. Poorly designed or operated HVAC systems can lead to inadequate ventilation rates, allowing the accumulation of pollutants, including volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), particulate matter (PM), and bioaerosols [1]. Additionally, the infiltration of outdoor air pollutants into indoor spaces can exacerbate IAQ challenges [2], especially in urban settings with high external pollution levels [3]. It is crucial to consider not only ventilation factors and the influx of external air pollutants but also additional elements such as the hospital's specific activities, occupancy patterns, the area or volume where sampling is conducted, and the materials comprising the furniture, paints, equipment, and the building itself [4].

Within this context, the FOTOAIR group at CIEMAT is devoted a depth characterization study of the indoor air pollutants in the framework of the European project K-HEALTHinAIR ("Knowledge for Improving Indoor Air Quality and Health"). This interdisciplinary research initiative aims to deepen the understanding of chemical and biological indoor air contaminants that impact health. Through a rigorous approach based on data collection in real-world environments, public health monitoring, and the analysis of particularly vulnerable groups, the project seeks to investigate correlations between indoor air quality characterization and its adverse health effects. Within this framework, air quality has been characterized in five areas of a hospital over the course of one year: Outdoor, Hall, Intensive Care Unit (ICU), Pathology Department, Waiting Room, and Hospitalization Ward. In parallel, continuous IAQ monitoring was carried out using air quality sensors, whose application and performance have been previously described and validated [5]. While these sensors present certain limitations inherent to the technology, they offer higher temporal resolution and enable the detection of dynamic events that may affect indoor air conditions. As such, they are proposed as a complementary tool to support interpretation and enrich the findings obtained from the main sampling campaigns, which remain the primary and most robust source of data in this study.

The results presented derive from the characterization of IAQ in the aforementioned areas of a hospital in Barcelona, with a comprehensive assessment of three contaminant categories: chemical pollutants, microbiological agents, and suspended particulate matter. Detailed findings will be provided regarding the presence of volatile organic compounds (VOCs), including the classification of the sampled areas based on total VOC (TVOC) concentrations, which range from 74.80 to 11.231 μg/m³. The concentrations of potentially harmful microbiological agents, such as bacteria and fungi, will also be reported. In addition, suspended particulate matter levels, known for their association with adverse health effects, will be measured. These data will enable an evaluation of the combined impact of these contaminants on hospital staff health and facilitate the identification of hospital zones where mitigation strategies could be implemented to reduce airborne pollutant exposure. This comprehensive study will make it possible to determine the most appropriate technology for efficient indoor air treatment—whether filtration, adsorption, or photocatalysis—depending on the specific characteristics of the pollutants identified.

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Acknowledgements

This work has received financial support from The K-HEALTHinAIR project, Grant Agreement nº 101057693, under a European Union's Call on Environment and Health (HORIZON-HLTH-2021-ENVHLTH-02).

F-28/P-28

Photocatalytic ring hydrogenation of furfuryl alcohol over cocatalyst-loaded TiO_2

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Recently, conversion of furfural and the related compounds derived from inedible biomass has been investigated extensively. However, many of them require severe conditions such as high temperature and/or high pressure. Since there is a need for more environmentally friendly reaction systems, we focused on a photocatalytic reaction, which can be operated under a mild condition. Previously, we found that furfural could be selectively hydrogenated to furfuryl alcohol (FOL) using titanium oxide (TiO_2) as a photocatalyst and alcohol as a hydrogen source under ambient temperature and pressure conditions [1]. On the other hand, hydrogenation of furan rings (ring hydrogenation) is difficult, i.e., Pd/TiO_2, which was effective in the ring hydrogenation of furan without functional groups, caused the decomposition of the hydroxymethyl group of FOL [2]. In this study, we prepared various kinds of TiO_2 with co-catalyst (M/TiO_2) and found that TiO_2 with Rh co-catalyst was effective for the ring hydrogenation of FOL.

1 wt% M/TiO_2 was prepared using the photodeposition method. TiO_2 (TAYCA, MT-150A) powder was suspended in 50 vol% methanol solution containing a metal source ($PdCl_2$, $RhCl_3$, $RuCl_3$, H_2PtCl_6, $HAuCl_4$, $AgNO_3$ or $CuCl_2$) in a test tube. Each test tube was photoirradiated using a high-pressure mercury lamp (KOIKE). M/TiO_2 (50 mg) was suspended in 5 cm^3 of methanol containing FOL (40 μmol) in a test tube, and then photoirradiated under argon (Ar) with the same high-pressure mercury lamp. For an adsorption experiment, M/TiO_2 (200 mg) was suspended in 5 cm^3 of methanol containing FOL (100 μmol) in a test tube, and then stirred under Ar in the dark.

Table shows the results of ring hydrogenation of FOL and adsorption experiments of FOL with M/TiO_2. In the case of unloaded TiO_2, ring hydrogenation of FOL and H_2 production did not occur. In the case of Ru, Pt, Au, Ag and Cu loaded TiO_2, hydrogenation of furan rings did not occur, while H_2 produced by proton reduction. In the case of Pd- and Rh-loaded TiO_2, ring hydrogenation of FOL occurred and the conversions of FOL were >99% and 62%, respectively. For metals other than Pd and Rh, the adsorption amounts were less than or equal to the amount of TiO_2, indicating that FOL was not adsorbed on these metals. These results indicate that the activity of ring hydrogenation is determined by the adsorption of FOL on the metal co-catalyst. In Pd/TiO_2, the selectivity of tetrahydrofurfuryl alcohol (THFA) was about 46%, while by-products, 2-methylfuran (2-MF) and 2-methyltetrahydrofuran (2-MTHF), were produced. In contrast, in Rh/TiO_2, the decomposition of hydroxymethyl groups was significantly inhibited, and the selectivity of THFA reached about 96%. The reason for the difference in selectivity between the two co-catalysts was investigated in detail.

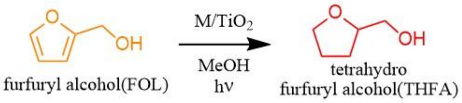

Table Results of photocatalytic conversion of FOL in methanolic suspensions of M/TiO_2 under irradiation of UV-light for 10 min and the amount of FOL adsorbed on M/TiO_2 (FOL_{ads}) in methanolic suspensions in the dark for 20 h.

M	Conv. / % (FOL)	Sel. / % (THFA)	Sel. / % (2-MF)	Sel. / % (2-MTHF)	FOL_{ads} / µmol
-	-	-	-	-	5.0
Pd	>99.0	44.5	45.9	3.0	6.9
Rh	61.8	95.8	1.3	0.0	10.4
Ru	-	-	-	-	2.7
Pt	-	-	-	-	5.2
Au	-	-	-	-	2.3
Ag	-	-	-	-	1.3
Cu	-	-	-	-	2.3

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F-29/P-29

Photocatalytic upcycling of PET into CH_4, H_2 and high-value liquid products

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In recent years, the consequences of fossil fuel overuse and the detrimental impacts on both environment and climate have become more prevalent than ever.[1] Efforts have been made to investigate sustainable alternatives for both energy and fuel generation. Within the photocatalytic community green hydrogen has gained great attention as it possesses a high energy density and can be generated solely with light and under ambient conditions.[2,3] Furthermore, the field of photoreforming has gained increasing recognition. This process involves the conversion of carbon containing waste (such as microplastics or biomass) into solar fuels and valuable chemicals by utilising light to drive chemical reactions.[4]

This study demonstrates the commercial potential of P25 TiO_2 towards photocatalytic upcycling of polyethylene terephthalate (PET) microplastics by systematic exploration of the effect of co-catalyst, reaction temperature and atmosphere on the generation of solar fuels and high-value liquid products. We demonstrate that while neat P25 yields minimal H_2 evolution, increasing the reaction temperature enhances its production significantly, and the addition of Pt further boosts H_2 generation by four orders of magnitude resulting in 15.35 µmol/h of H_2 and apparent quantum yield (AQY) values up to 0.45 %. On par with H_2, we observe generation of CH_4 from the reaction mixture, which we conclude to originate directly from PET rather than hydrogenation reactions. Liquid-phase analysis reveals diverse oxidation products, including acetic acid, oxalic acid, and ethanol, with selectivity influenced by catalyst composition and reaction conditions. The feasibility of large-scale application of the process is further validated through prolonged irradiation tests using solar-simulated light and an upscaled setup, which demonstrate remarkable AQYs reaching 0.84 %. These findings commence PET photoreforming as a promising route for producing solar fuels and valuable chemicals, paving the way for sustainable plastic processing and upcycling.

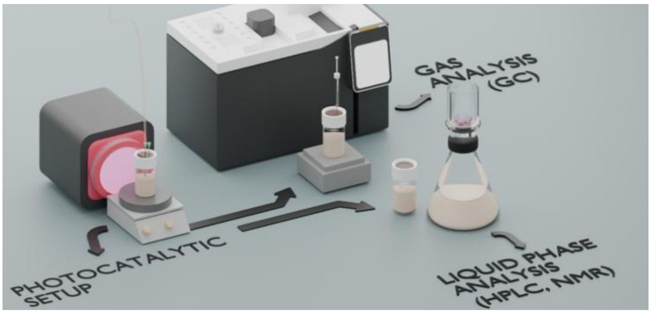

Fig. 1. Schematic illustration of the experimental protocol followed to conduct the photoreforming studies.

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Acknowledgements
This work has received financial support from the Austrian Science Fund (FWF, Project P32801 and Cluster of Excellence MECS).

F-30/P-30

Photoelectrocatalysis: A sustainable solution for Resource Recovery from wastewater

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Along with the environmental pollution, the rising demand for energy has become a significant environmental threat. As a rich source of nutrients, metals, and energy, wastewater presents great potential for resource and energy recovery [1]. Photoelectrocatalysis (PEC) has gained significant attention as an innovative technique for eliminating pollutants and recovering resources recovery from wastewater[2]. Various electrodes have been explored for wastewater treatment and resource recovery, including TiO_2, $BiVO_4$, C_3N_4, as well as materials like WO_3 and Fe-based compounds[3,4]. These semiconductors are favored for their effectiveness, affordability, and potential in various applications. In PEC cells, key parameters such as electrode type, cell potential, current density, and pH critically impact the efficiency of the process[5]. The primary goal of this study is to examine the potential of nanoengineered electrodes in a photoelectrochemical reactor to break down organic contaminants, including contaminant of emerging concern, CECs, and concurrently extract valuable resources such as hydrogen, as a clean energy, nutrients such as phosphate, and metals from wastewater. Initial research focused on utilizing titania nanotube photoanodes, created by anodizing titanium metal in the presence of fluoride ions. The morphology and presence of nanotubes were confirmed using FE-SEM analysis. The photoanodes were tested for photocurrent response. In addition, we explored combining electrochemically-assisted precipitation to collect precipitated materials, with the goal of removing phosphate from wastewater and recovering calcium phosphate for use as fertilizer. Future investigations will address the anode and cathode reactions, and on designing two-compartment photoelectrochemical cells to remove contaminants and enhance energy and resource recovery.

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Acknowledgements

Authors would like to give special thanks to Ulster University for the financial support for SA.

F-31/P-120

Characterization of lead-free Cs_2SnI_6 perovskite and its ecotoxic effects on isopods

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$CsPbX_3$ semiconductor perovskites are considered as a promising material in the research and the development of new types of solar cells. However, its lead-related toxicity raises several concerns, such as oxidative stress, carcinogenicity, developmental toxicity. One of the possibilities to reduce their toxicity is by replacing Pb with other metallic elements.

In the present work, Cs_2SnI_6 lead-free perovskite was synthesized by solvothermal method at different temperatures (120 °C, 150 °C and 180 °C) with the aim to investigate the environmental impact of the differently synthesized nanoparticles. The material structure, morphological and optical properties of the samples were characterized by XRD, SEM and DRS material analysis methods.

The samples were stable in air for the duration of the test, but in contact with water, a rapid decomposition followed, and the material lost its crystal structure. This process was partially reversible, as the material recrystallised from its medium after drying. Further dissolution-crystallization sequences also resulted in a decrease in crystallinity, due to the loss of iodine content, and the material contained increasing amount of CsI.

An important criterion for environmentally stable materials is that they retain their original form in different media. For unstable materials, the release of various chemical species may be responsible for toxicity, therefore it is of particular importance to investigate the effects of these on the environment.

In the toxicological experiment, habitats with increasing concentrations of a selected sample were established to monitor the population changes of the isopods (*Porcellio laevis*) and the stability of the released material in the environment. The protocol was to follow the life cycle of 15 individuals (10 adults and 5 developing individuals) for one month. The soil was amended with 0, 0.1, 0.5 and 1.5 wt% perovskite and the living conditions (soil thickness, water, food source, calcium source) were adapted to the species. No mortality occurred in the control experiment (0 wt%). Significant declines in numbers were observed in the 0.1 and 0.5 wt% experiments, and 100% mortality in two weeks in the 1.5 wt% experiment.

Acknowledgements
The authors are grateful for the financial support of the 2021-1.2.6-TÉT-IPARI-MA-2022-00009 project.

F-32/P-32

Photothermal valorisation of CO_2 into methanol over $Cu/ZnO/Al_2O_3$

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The conversion of CO_2 into products of interest in the energy and chemical sectors, is considered a promising solution to address the growing demand for energy and reduce CO_2 emissions. In this work, we propose the synergistic combination of thermal and photonic (photothermal) catalyst activation to improve both energy efficiency and performance under milder operating conditions in methanol (MeOH) synthesis from CO_2 and H_2. A series of $Cu/ZnO/Al_2O_3$ catalysts have been selected as promising candidates for photothermal catalysis as these systems achieve high levels of conversion and selectivity to MeOH in CO_2 hydrogenation through thermal activation, but require high temperature and pressure [1], and the copper and zinc phases also present optical activity by generating e^-/h^+ pairs that can participate in charge transfer processes modifying the activity.

$ZnO\text{-}Al_2O_3$ support was prepared by microemulsions method, incorporating Al_2O_3 (Aldrich) in the final microemulsion. The resulting solid was dried and calcined at 400 ºC. Different CuO loadings were incorporated by impregnation with a copper salt. Electronic and structural properties were analysed by different characterisation techniques: N_2 adsorption/desorption isotherms, elemental chemical analysis ICP-OES, UV-visible absorption, X-ray diffraction (XRD) and *in situ* X-ray absorption spectroscopy (XAS) during temperature programmed reduction (H_2-TPR). The catalytic activity tests were performed at ambient pressure using a glass tubular reactor that allows heating and lighting simultaneously. The gas mixture, $H_2 + CO_2$ ratio 1:3, was fed with a total flow of 40 ml/min and the reaction products were analysed by gas chromatography at different temperatures (200 - 400 ºC) while applying light ON/OFF cycles. The influence of a pre-reduction treatment of the catalyst was also analysed. Mechanistic insights were obtained through, *operando* near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) using different gas mixtures and light ON/OFF cycles, and *operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled with the periodic modulation of external illumination (light ON/OFF cycles). Application of modulated excitation spectroscopy (MES) with phase-sensitive detection (PSD) to DRIFT spectroscopy has proven potential for the detection of reaction surface intermediates and their discrimination from reaction spectators, providing sensitive and selective information for mechanistic and microkinetic studies.

The main products of the thermal reaction were MeOH and CO. The latter is due to the reverse water gas shift reaction, RWGS, favoured at high temperatures and low pressures. Cu content modulates the activity (Figure 1A) and the catalyst with intermediate Cu loading presents the highest yield and selectivity to MeOH. Moreover, the reduction pre-treatment led to a broader temperature window where MeOH was produced and an improvement in its selectivity, although conversion decreased (Figure 1B). In addition, light had a positive effect on both activity and selectivity, improving total CO_2 conversion and favouring MeOH production.

This change cannot be explained only by thermal effects, suggesting that light is also inducing charge transfer processes that favour MeOH production. Furthermore, the improvement in MeOH production was suppressed when applying visible light, while CO enhancement was maintained, which implies different effects in the reaction mechanism depending on the wavelength used. The electronic properties of the active centres were studied by in situ XAS during TPR. Different redox properties as a function of the Cu content were observed: increasing %Cu led to a faster reduction and decreases the amount of intermediate species Cu^+. Characterisation under reaction conditions by NAP-XPS experiments showed light induced charge transfer phenomena between Zn and Cu centres. It was also possible to analyse the species adsorbed on the surface of the catalyst and their evolution as a function of the reactive atmosphere, temperature and light. MES-PSD DRIFTS experiments confirmed the NAP-observations and provided complementary information on the reaction mechanism and how light interferes.

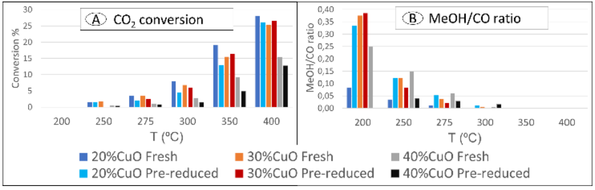

Fig. 1. A) Conversion of CO_2. B) Ratio between methanol and CO production.

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Acknowledgements

Funded by MCIN/AEI/10.13039/501100011033 (Project PID2020-118593RB-C21).

Remediation of Indoor Air Quality through Photocatalytic VOCs Removal on construction materials

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Indoor air quality (IAQ) has become an increasing concern due to the presence of volatile organic compounds (VOCs), which can cause health problems such as irritation, respiratory issues, and long-term effects on the nervous system [1]. Photocatalytic oxidation has emerged as a promising method for removal VOCs, offering a potential method to enhance IAQ [2]. In this work, different type of photocatalysts, exhibiting different colours, were implemented on different construction materials and were tested under different irradiation sources [3] evaluating the removal of VOCs by the different photocatalytic systems. As VOCs emitters, a variety of common household products—cleaners, insecticides, and air fresheners— have been used. VOC concentrations were measured using a photoionization sensor (VOC-TRAQ) and mineralization were monitored by measuring CO_2 formation. The influence of key environmental and experimental parameters, such as temperature, humidity, and flow rate on the photocatalytic processes, as well as the potentiality of this technology for this application, are analysed and the discussed.

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F-34/P-34

Shaping Nanocrystals to Understand Catalysis: Case Study of Fe_2O_3 and In_2O_3

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Faceted metal oxide nano/microcrystals have gained significant attention in fields like sensing, catalysis, and energy conversion. Recently, the focus has shifted to the exposed facets of these crystals, which are more critical for achieving enhanced catalytic performance compared to other characteristics such has their size, or shape. However, a major challenge in harnessing facet-dependent performance lies in the successful synthesis of polyhedral crystals with well-defined Miller index facets. Each facet exposes a unique atomic arrangement, and it directly influences surface energy, electronic structure, and reactivity, ultimately impacting the catalytic behaviour. Metal oxide crystals have different facets depending on their Miller indices, which can be categorized into low-index and high-index facets. Low-index facets, such as (001), (111), and (110), are more thermodynamically stable, however featuring less reactivity, while high-index facets, like (012), have higher surface energy, making them more reactive and offering more active sites. Achieving a balance between these properties is essential for designing materials that optimize both performance and durability in photo/electrochemical (PEC) water splitting, CO_2 reduction and alcohol oxidation reactions [1].

Faceted metal oxides, particularly indium oxide (In_2O_3) and iron oxide (Fe_2O_3), are crucial in various applications, including catalysis, energy storage, and photoelectrochemical processes [2]. In our work, we successfully synthesized Fe_2O_3 (hematite) cubes with exposed (012) facets and In_2O_3 cubes using a solvothermal method (**Fig. 1**) [3], [4] and characterized by SEM, HRTEM and temperature dependent XRD. Both nanostructures feature narrow size distribution and high uniformity, which has been difficult to achieve before. We further explore photocatalytic properties of the Fe_2O_3 cubes towards light-driven alcohol oxidation, primarily focusing on methanol oxidation. In future work, we plan to utilize faceted-In_2O_3 cubes modified with co-catalytic Pd, Ag, etc. for electrochemical CO_2 reduction. Overall, these findings offer valuable insights into the design of faceted-In_2O_3 and Fe_2O_3 materials for advanced energy and environmental applications while also bridging the “materials gap” important to connect surface science and real-world applications [5].

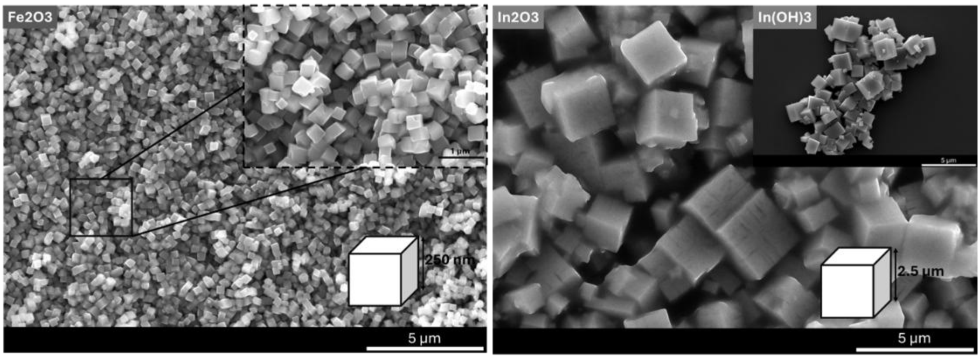

Fig. 1. SEM images of (012) Fe_2O_3 and In_2O_3 with average size of 250 nm and 2.5 µm respectively.

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This work has received financial support from FWF Cluster of Excellence "Materials for Energy Conversion and Storage" (MECS, 10.55776/COE5).

F-35/P-35

Sol-gel Synthesis of $SrTiO_3$ Enables Enhanced Overall Water Splitting Activity by Al/ Ga doping and *in-situ* formation of a $SrTiO_3/SrCO_3$ heterojunction

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Photocatalytic overall water splitting is regarded as a promising approach for green hydrogen generation. Despite over 50 years of research on various materials, fundamental catalytic research is still indispensable to understand important details in photocatalytic systems. $SrTiO_3$ is a prominent photocatalyst and benchmark material due to its suitable band edge positions and versatility regarding aliovalent doping [1]. Recently, immobilized Al:$SrTiO_3$ particles have been used on a 100 m^2 scale for green hydrogen generation under solar light irradiation [2]. Despite first steps towards commercialization, research on $SrTiO_3$ materials has mainly focused on simple (nano)particulate systems. From a synthetic point of view, morphological diversity is difficult to achieve due to high calcination temperatures. Therefore, porous $SrTiO_3$ materials or other advanced morphologies have only been studied poorly. Molten-salt syntheses have been dominating the field because of high crystallinity of the resulting materials and tuneable facet exposures [3]. However, side phases like the layered perovskites Sr_2TiO_4 or $Sr_3Ti_2O_7$ might form at calcination temperatures close to 1000°C [4]. Furthermore, $SrCO_3$ is an ubiquitous surface species on $SrTiO_3$ and common in syntheses that use an excess of strontium precursor [5].

Herein, we present a new sol-gel synthesis that allows for more control over doping rates, targeted $SrCO_3$ side phase formation, and lower calcination temperatures. Not only is this approach reducing the energy uptake during calcination by 71%, we also show that a $SrCO_3$ side phase leads to an increase in photocatalytic overall water splitting activity under UV light irradiation. We attribute this increase to the formation of a $SrTiO_3/SrCO_3$ heterojunction. However, the effect can be overlooked very easily due to low amounts of carbonate present on most $SrTiO_3$ samples and the low but relevant solubility of $SrCO_3$ in water.

Moreover, aliovalent doping of $SrTiO_3$ at the Ti^{4+} lattice position with either Al^{3+} or Ga^{3+} ions can be studied precisely by adding suitable Al or Ga precursors to the initial sol. Interestingly, both dopants show a very similar influence on the photocatalytic activity. Higher amounts of dopants ultimately lead to a $SrCO_3$ side phase and a sudden increase in photocatalytic overall water splitting activity.

Furthermore, our findings include results on porous $SrTiO_3$ materials and show that doping is possible at calcination temperatures as low as 550 °C. Overall, these results fill important gaps in $SrTiO_3$ research and contribute to greater morphological diversity in the future.

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L. S. acknowledges financial support from the FCI (Fonds der Chemischen Industrie, Kekulé Scholarship). Furthermore, L. S. acknowledges support from the Elite Study Program Macromolecular Science within the Elite Network of Bavaria (ENB) and support from the BayNAT program within the UBTGS (University of Bayreuth Graduate School).

F-36/P-36

Stability of $CuBi_2O_4$ Photocathodes for Solar-Driven Reduction Reactions

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The development of p-type semiconductor photoelectrodes is gaining increasing attention as they have an important role in sustainable energy conversion, namely photoelectrochemical (PEC) water reduction. Among them, $CuBi_2O_4$ appears to be promising photocathode material for solar-driven reduction reactions due to its suitable bandgap (~1.8 eV) and exceptionally positive photocurrent onset potential (> 1 V vs RHE). Additionally, it is composed of earth-abundant elements and exhibits favourable optoelectronic properties for visible light harvesting. The essential material properties of $CuBi_2O_4$ photocathodes, relevant to PEC water splitting (light optical absorption, charge carrier transport, reaction kinetics and stability), were recently reported by Berglund et al. [1], e. g. flatband potential ~1.275 V vs RHE and light penetration depth of 244 nm (for light at 550 nm). In Na_2SO_4 electrolyte solution, $CuBi_2O_4$ undergoes reductive photocorrosion, which limits its use as a proton-reducing photocatalyst [2].

In this work, we investigated the photoelectrochemical properties of $CuBi_2O_4$ photocathodes. PEC measurements, as well as stability experiments were conducted in 0.1 M Na_2SO_4 electrolyte saturated with various gases (O_2, air or N_2). First, the conduction band potential was calculated and critically evaluated with respect to the possible reduction of various species in the electrolyte (MV^{2+}, O_2 ($2e^-$), O_2 ($4e^-$), H_2O_2) or semiconductor itself. Particular attention was given to the two-electrode oxygen reduction reaction (ORR), which enables the production of hydrogen peroxide (H_2O_2). Such reduction reaction has not yet been studied in detail, on the contrary, H_2O_2 has been reported as an electron scavenger [3]. **Fig. 1** shows that the long-term stability of $CuBi_2O_4$ under irradiation (100 mW cm^{-2}) was highly sensitive to the type of gas with which the electrolyte was saturated. Under oxygen bubbling, the photocurrent remained nearly constant over one hour irradiation, indicating stable photoelectrocatalytic activity. Air saturation resulted in an initial slight decrease in photocurrent, followed by its stabilization. In contrast, nitrogen saturation led to rapid photocurrent decrease, suggesting partial degradation or deactivation of the $CuBi_2O_4$ photoelectrode over time. In this respect, $CuBi_2O_4$ shows better performance than Cu_2O, where even oxygen concentration corresponding to air bubbling was not sufficient to eliminate the self-reduction of Cu_2O to Cu and maintain the stable photocurrent [4].

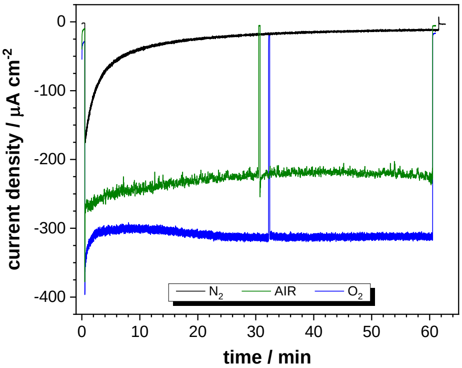

Fig. 1 Time dependence of current density of $CuBi_2O_4$ photocathode at −400 mV vs Ag/AgCl, Pt sheet as a counterelectrode. The electrolyte 0.1 M Na_2SO_4 was saturated with various gases (O_2, air or N_2). The irradiance was 100 mW cm^{-2} (AM 1.5).

The Faradaic efficiency of the two-electron reduction of O_2 to H_2O_2 was evaluated. The influence of factors such as the applied potential, electrolyte composition and/or surface modification (Au co-catalyst or heterojunction with g-C_3N_4) was investigated.

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This work was supported by the project "The Energy Conversion and Storage", funded as project No. CZ.02.01.01/00/22_008/0004617 by Programme Johannes Amos Comenius, call Excellent Research.

F-37/P-37

The influence of Ti_3C_2 MXene concentration on the photoactivity of P25

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In the current work, we focused on the synthesis of Ti_3C_2 MXene and its impact on the photocatalytic activity of benchmark reference P25 TiO_2. First, an in-situ method was attempted to produce HF to synthesize MXenes, but the product was unfortunately contaminated. The highest yield (78%) and satisfactory purity was achieved by mixing the precursor powder in a 40% HF solvent during the hydrothermal synthesis (Fig. 1.a) [1]. The products were then heated at 60 °C for 24 h, washed with distilled water, and dried under vacuum. The precursor was Ti_3AlC_2 in all cases.

After successfully obtaining the Ti_3C_2 MXene, a physical mixture was prepared with P25 TiO_2 at various mass concentrations and examined the evolution of photocatalytic performance of the samples. The model pollutant was phenol. Preliminary findings indicate that there is an optimal Ti_3C_2 concentration which enhances the activity of P25 (Fig. 1.b). The samples, which are containing in one and five mass concentration Ti_3C_2 degraded the model pollutants concentration nearly two times faster, than the P25 alone.

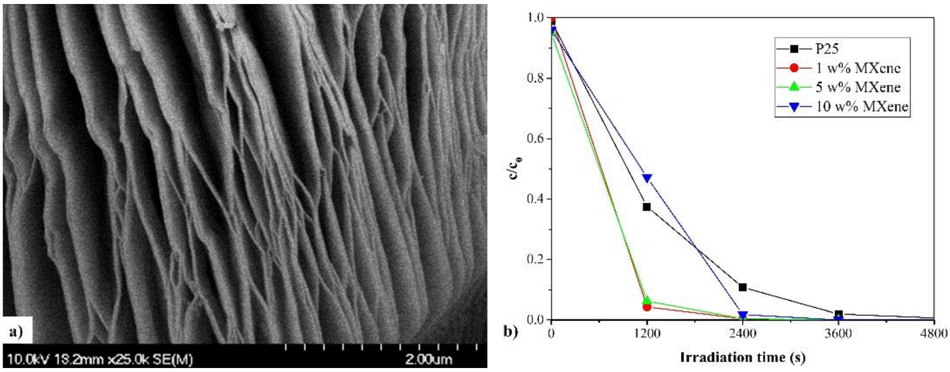

Fig. 1. SEM picture of the synthesized Ti_3C_2 MXene (a) and photocatalytic degradation of phenol (b).

After investigating the physical mixture of Ti_3C_2 MXene–P25 TiO_2 composites, the attention of the present work shifted to determine whether similar outcomes can be achieved by establishing chemical bonding between the composite components. For this purpose, another set of composites was prepared by sol-gel synthesis. The amorphous products were calcined in a tube furnace at 500 °C for 4 hours in oxygen atmosphere.

The effect of modifying P25 with Ti_3C_2 prepared via atomic layer deposition (ALD) will also be investigated. The samples will be further characterized using XPS, SEM, IR, and Raman measurements. Last, the ecotoxicology of the will be tested on isopods.

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Acknowledgements

Áron Ágoston acknowledges the Doctoral Student Scholarship Program of the Co-operative Doctoral Program (EKÖP-KDP-24-SZTE-6) of the Ministry of Innovation and Technology financed from the National Research, Development and Innovation Fund.
This project was supported by 2021-1.2.6-TÉT-IPARI-MA-2022-00009.

TiO_2 NB/Bi_3O_4Br Z-scheme heterojunction for photocatalytic degradation of paracetamol

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The presence of pharmaceuticals, such as paracetamol in wastewater has become a significant issue, exacerbated by a 198% increase in paracetamol consumption during the COVID-19 pandemic [1]. Photocatalysis is effective for removing paracetamol, with titanium dioxide (TiO_2) being a common photocatalyst due to its unique properties. However, the wide band gap of TiO_2 limits its activation [2]. Bismuth-rich oxybromides exhibit visible light activity, and Bi_3O_4Br, identified as one of the most effective photocatalysts in our previous study [3], was selected to form a heterojunction with TiO_2 nanobelts to enhance photocatalytic performance.

TiO_2 nanobelts (NB) were synthesized using the alkali-hydrothermal method, starting with 1 g of P25 TiO_2 powder dispersed in a 10 M NaOH solution. The mixture was treated hydrothermally at 180°C for 24 hours and then calcined at 600°C for 2 hours to crystallize the nanobelts. To synthesize the TiO_2 NB/Bi_3O_4Br composite, $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in ethylene glycol, mixed with a KBr solution, and combined with TiO_2 NB to form a suspension. NH_4OH was added, and the mixture was heated at 160°C for 18 hours in an autoclave. The resulting solids were washed with deionized water and ethanol, then dried at 80°C for 24 hours. The composite was prepared at varying ratios and analyzed using XRD, BET, FTIR, Raman, XPS, FESEM, EDX, XRF, UV-Vis DRS, PL, and EIS.

Prepared TiO_2 nanobelts have monoclinic structure. Raman and XPS analyses confirm strong interactions between Bi_3O_4Br and TiO_2 NB, with shifts in binding energies and spectral overlaps supporting the formation of a heterojunction. FESEM studies show even distribution of Bi_3O_4Br nanosheets and TiO_2 nanobelts (Fig. 1a). UV-Vis DRS results show improved visible light absorption and narrower bandgaps in Bi_3O_4Br/ TiO_2 NB composites compared to pure TiO_2 NB. The composite with the ratio of 2:1 (Bi_3O_4Br:TiO_2) was the most effective in paracetamol removal. This was due to the enhanced charge carrier separation, efficient charge transfer, and slower electron-hole recombination, as confirmed by PL (Fig. 1b), EIS (Fig. 1c), and time-resolved PL (Fig. 1d). The neutral pH of paracetamol (6.5) was optimal for degradation and 89 % removal efficiency was obtained. Increasing photocatalyst dosage up to 0.4-0.5 g/L improved removal efficiency to 96 % without hindering light penetration. However, higher initial pollutant concentrations decreased efficiency, resulting in 89 % removal at 10 mg/L and 55 % at 20 mg/L. Temperature increase enhanced degradation, with optimal performance reached at 35 °C (97 % removal efficiency). The results of stability and recyclability experiments showed that the composite retained 66% removal efficiency after four cycles, and structural stability was maintained as confirmed by XRD and FTIR analyses. The mineralization degree of paracetamol was tested by total organic carbon (TOC) analysis. It was found that around 54 % and 70 % of TOC was eliminated when the 0.2 g and 0.4 g of photocatalyst was used. The TOC experiments were done at neutral pH of paracetamol, 10 mg/L of paracetamol, room temperature, and without presence of any scavengers.

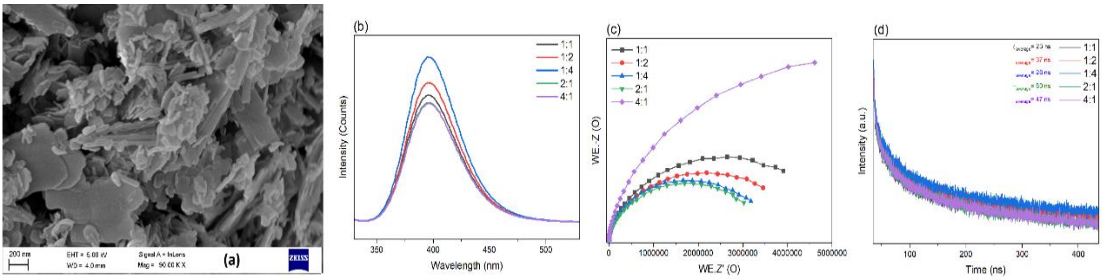

Fig. 1. (a) FESEM, (b) PL, (c) EIS, and (d) time-resolved PL.

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Water based green sol-gel synthesis of TiO_2 sol for photocatalytic water and air purification coatings with self-cleaning nature

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Environmental pollution is a pressing concern of modern society, as air, water and soil contamination caused by progressing industrial societies are directly affecting the ecosystem. The European Union (EU) is also committed for a sustainable environment by reducing the pollution to safe levels for human health and ecosystem. The EU Green Claims Directive [1] and EU Green Deal vision 2050 [2] raise critical concerns for sustainable science of materials as it strict the verification rules under the EU Green Claims Directive to use economic and eco-friendly processes and protocols for materials synthesis. In pursuit of sustainable environmental remediation technologies, TiO_2 photocatalyst coatings have garnered significant interest of both industrial and researcher community. Numerous methods have been employed by researchers for synthesis of TiO_2 based coatings for environmental remediation. However, most of these methods involve harmful reagents such as organic solvents, strong acid catalysts and some other additives which pose a serious threat to both human health and ecosystem [3].

This research presents the effect of temperature and aging time on green sol-gel synthesis of TiO_2 sol for the preparation of highly uniform and adherent coating. Titanium tetraisopropoxide (TTIP) was used as the precursor, with water as solvent/hydrolysing agent and acetic acid as catalyst/chelating agent serving as eco-friendly reagents under mild conditions. TiO_2 layers were immobilized on glass substrates via dip-coating technique, evaluating their properties for Rhodamine B photooxidation in water and formaldehyde in gas phase under UV-A irradiance. Moreover, the self-cleaning properties were evaluated according to ISO 27448:2009 standard by the photodegradation of oleic acid under UV-A exposure [4]. The results revealed a critical sensitivity of the TiO_2 sol to ambient conditions, which significantly affected sol aging behaviour, quality and photocatalytic activity of coatings. TiO_2 sols synthesized at ambient conditions between 26-32 ℃ characteristic of summer season in Mediterranean countries and aged progressively, developed sufficient stability and activity after 21 days. DLS revealed formation of nanoparticles (10-100 nm) in these sols with an increasing trend over aging time indicating particles growth and colloidal instability. These sols yielded highly uniform and efficient coatings with excellent photodegradation of Rhodamine B. Conversely, when the synthesis method was performed at temperatures ranged between 15-18 ℃ during winter season, the resulting sols remained low viscous leading to inefficient coatings with lower amount of TiO_2 (≤ 0.026 mg/cm^2). DLS confirms the presence of nano scale particle distributions. Various attempts to get efficient coatings were unsuccessful even by increasing TiO_2 amount and varying layer drying or the annealing temperature.

To overcome this issue, an accelerated aging protocol was opted by incubating the sol at 40 ℃ for 21 hours. This controlled heating triggered partial oligomerization with, increasing the viscosity of the sol, leading to formation of homogeneous and adherent coatings with 0.106 mg/cm^2 amount of TiO_2. A single-layer coating of this sol exhibited exceptional degradation of formaldehyde in gas phase (10 ppm) under UV-A irradiance with 100%, 73%, and 56% removal at 300, 500, and 700 mL.min^{-1} flow rates, respectively. All coatings showed a photoinduced super hydrophilic behaviour with the water contact angle measurements with values below 10° after 180 min under UV-A exposure, confirming effective surface activation and strong self-cleaning nature. These findings underscored the critical connection between aging conditions and sol rheology properties for fabrication of efficient photoactive coatings.

This study emphasizes on temperature-mediated aging as a decisive factor for reproducibility and performance of green sol-gel derived TiO_2 coatings. The proposed strategy of accelerated aging supports a simple and scalable route to prepare TiO_2 based green photocatalytic materials for indoor air purification and other environmental remediation technologies.

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This study was carried out within the MICS (Made in Italy —Circular and Sustainable) Extended Partnership and received funding from the European Union Next–Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 - D.D 1551.11-10-2022, PE00000004) and MCIN/AEI Spain (PID2022-138682OB-I00).

F-40/P-40

Photocatalytic destruction of Escherichia coli in water using slurry and rotating-disk photocatalytic reactors

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The application of photocatalysis for the disinfection of water has been extensively reported over the past 30 years. Titanium dioxide (TiO_2) has been the most widely and successfully used photocatalyst to date; however, it is not without its limitations. Frequently observed long lag times, sometimes up to 60 min, before bacterial inactivation begins and the presence of residual microorganisms, for example, up to 104 colony forming units, remaining after treatment are ongoing challenges with this particular photocatalyst. It is therefore important to find alternative photocatalysts that can address these issues. In this study, we compared the disinfection capacity of TiO_2 with that of zinc oxide (ZnO) using Escherichia coli as a model organism in both a suspended and immobilized catalyst system. Our results showed that ZnO was superior to TiO_2 in a number of areas. Not only were bacterial rates of destruction much quicker with ZnO, but no lag time was observed prior to inactivation in suspended systems. Furthermore, complete bacterial destruction was observed within the treatment times under investigation. The greater efficiency of ZnO is believed to be due to the decomposition of the bacterial cell wall being driven by hydrogen peroxide as opposed to hydroxyl radicals. The results reported in this paper show that ZnO is a more efficient and cost-effective photocatalyst than TiO_2 and that it represents a viable alternative photocatalyst for water disinfection processes.

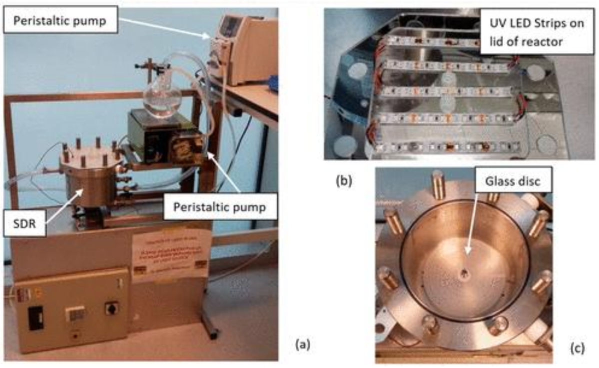

Fig. 1. a) SDR. A peristaltic pump circulates the water around the vessel and cooling water around the water jacket. (b) UV LED strips attached to the bottom of the lid of the reactor. (c) Image of the internal view of the SDR with a TiO_2-coated disk held in place by the central metal rod.

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Acknowledgements

This work has received financial support from the EPSRC & China Scholarship Council No. 201806030133)

Poster communications

Effect of silver deposition on the material characteristics and photocatalytic activity of barium titanates

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Silver (0–5 wt%) was reduced on the surface of barium titanates ($BaTiO_3$) to investigate their effect on the properties and photocatalytic activity of the support. The samples were characterized by X-ray diffractometry, diffuse reflectance spectroscopy, photoluminescence (steady state and time-resolved), transmission electron microscopy, linear sweep voltammetry, and X-ray photoelectron spectroscopy. Their photocatalytic activity was evaluated by phenol degradation under UV light irradiation. A commercial $BaTiO_3$ without silver was used as a reference. Nominal silver amounts were consistent with the measured ones in the samples containing 0–3 wt% silver; however, at high nominal amounts (4–5 wt%), the measured silver content was decreased significantly (~1.3 wt%). Samples containing larger silver particles had higher photoactivity than samples containing smaller silver particles. The sample containing 5 wt% silver performed the best, reaching a phenol degradation rate of 2.15×10^{-4} s^{-1}, over an order of magnitude higher than that for the non-silver-containing reference sample (1.48×10^{-5} s^{-1}). The enhanced photoactivity was associated with the larger silver particles covering less of the $BaTiO_3$ surface, leaving more active sites available, and with the silver hindering charge recombination by trapping the electrons and thus increasing the efficiency of holes.

Acknowledgements

Áron Ágoston acknowledges the Doctoral Student Scholarship Program of the Co-operative Doctoral Program (EKÖP-KDP-24-SZTE-6) of the Ministry of Innovation and Technology financed from the National Research, Development and Innovation Fund. The authors are grateful for the financial support of the 2021-1.2.6-TÉT-IPARI-MA-2022-00009 project. Tamás Gyulavári acknowledges the NKFI-PD-138248 project, the Bolyai János scholarship (BO/00447/23) provided by the Hungarian Academy of Sciences, and the ÚNKP-23-4-II New National Excellence Program of the Ministry for Culture and Innovation from the source of the National Research, Development and Innovation Fund. Project no. TKP2021-NVA-19 has been implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-NVA funding scheme.

Charge-Carrier Dynamics and Surface Active Sites in Ferrite Thin Films

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In the pursuit of sustainable technology and energy transition, photo(electro)catalytic (PEC) CO_2 conversion presents a promising strategy for utilizing renewable energy to mitigate climate change [1]. However, a key challenge limiting efficiency is the rapid recombination of photo-generated charge carriers at low external bias [2]. Constructing direct Z-scheme heterojunctions has proven effective in extending charge carrier lifetimes to 10–100 ns [3], enhancing catalytic performance. This project aims to improve CO_2 photo(electro)conversion efficiency by addressing gaps in understanding real-time charge dynamics and surface activity in Z-scheme catalytic powders and films. To elucidate the impact of morphology and extent of heterojunction contacts, $ZnFe_2O_4$@TiO_2 nanocomposite powders with different $ZnFe_2O_4$ morphologies and varied TiO_2 to $ZnFe_2O_4$ wt.% ratios were first synthesized and then characterized by XRD, Raman, FTIR, DR, SEM-EDS, XPS, etc.

To examine the impact of TiO_2 morphology on PEC performance, we will next fabricate and characterize photoelectrode films on two Ti-based supports: (1) Untreated Ti foil, with a dense layer of $ZnFe_2O_4$@TiO_2 nanoparticles, and (2) Treated Ti foil, which has TiO_2 nanotubes grown on its surface before depositing $ZnFe_2O_4$. Time-resolved PL spectroscopy will track charge carrier dynamics, while DMPO spin-trapping EPR will analyze reactive species under visible-light irradiation, with and without electrical bias, in different solvents. Finally, the photocatalytic activity of powders and selected films will be evaluated. If successful, this work could drive advancements in renewable energy utilization for sustainable chemical production, significantly contributing to climate change mitigation.

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This work has received financial support from the European Research Executive Agency under the action HORIZON TMA MSCA Postdoctoral Fellowships - European Fellowships, project 101204943 - PROSCOPY.

P-43

The effect of Ag concentration and film roughness on the photocatalytic activity of self-cleaning spin-coated Ag/TiO_2 Films

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To date, titanium dioxide (TiO_2)-based self-cleaning coatings on glass substrates that decompose the organic pollutants from the glass surface through their photocatalytic and hydrophilic properties have attracted significant interest [1]. TiO_2 has been known as the ideal semiconductor for self-cleaning applications due to its activity under UV, its stability, low toxicity, low cost, and ease of deposition. However, its relatively large band gap (~3.2 eV) limits sunlight absorption, and the rapid recombination of photogenerated (e^-/h^+) pairs reduces efficiency. To address these challenges, doping TiO_2 with foreign elements, such as silver, has been explored to reduce recombination rate, lower the band gap, and thus enhance visible light absorption [2]. This study investigates the role of Ag on the activity of TiO_2 films towards the decomposition of stearic acid, focusing on how the Ag loading and varying the deposition parameters influence the film's roughness and thickness and, thus, the photoactivity.

TiO_2 films were doped with various amounts of Ag (0.1, 0.5, 1, 1.5, 2, and 5 wt%) synthesized via sol-gel spin coating and employed for the photocatalytic oxidation of stearic acid. The 1.5 wt% Ag/TiO_2 film roughness and thickness were changed by applying a range of spin speeds (500-7000 rpm) and also by sequentially depositing one to ten layers on top of one another. Fourier transform infrared (ATR-FTIR) spectroscopy was used to monitor stearic acid concentration before and after UV illumination. X-ray photoelectron spectroscopy (XPS) and photo-induced force microscopy (PiFM) were used to characterize the coatings and to quantify any remaining stearic acid after photocatalysis. XRD and DRS-UV spectroscopy were also used to characterize the coatings.

Fig. 1. (a) shows that incorporating Ag into TiO_2 films enhances the photocatalytic activity. The 1.5 wt% Ag film exhibits the highest photoactivity. In contrast, TiO_2 films doped with the highest amount of Ag (5 wt%) are less active than undoped films. The catalytic coatings demonstrate excellent reusability and long-term stability for at least three cycles without any treatment or washing between cycles, as shown in Fig.1. (b).

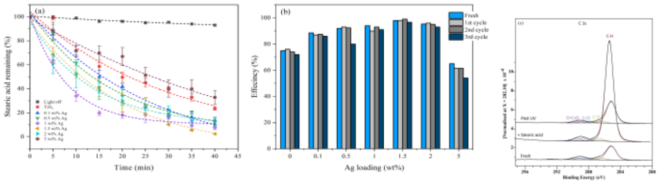

Fig. 1. (a) Effect of Ag loading on the activity of TiO_2 films; (b) reusability test; (c) XP spectra of photocatalytic behaviour of 1.5 wt% Ag/TiO_2 coating.

XRD and DRUV-Vis data confirm that all films consist of anatase only, and there is no significant variation in the band gap after loading different amounts of sliver.

XPS and PiFM indicate that there is no remaining stearic acid on the 1.5 wt% Ag-doped TiO_2 surface after the reaction. The C 1s XP spectra, Fig.1. (c), showed that a significant amount of carbon is removed from the surface after photocatalysis and the PiFM data confirmed that the rapid decomposition rate of stearic acid is attributed to the adsorption of the carboxylic functional group to the photocatalyst surface. Water contact angle results reveal that the photocatalytic coatings are hydrophilic even after being exposed to a 365 nm LED light for 60 min.

Increasing the spin speed from 500 to 7000 rpm reduced the film thickness from 20 to 120 nm. According to our findings, changing the spin speed affects the film thickness but has no noticeable impact on the photoactivity. In contrast, spin coating 1 to 10 layers at 3000 rpm raised the surface roughness from 2.7 to 8.4 µm and a trend of decreased photocatalytic reaction rate for rougher films (RMS roughness > ca. 3 µm) was observed.

This study concludes that optimising film roughness and doping with a catalyst such as silver, rather than adjusting the thickness, is the most effective approach for producing practical self-cleaning coatings.

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A Dual-Function $BiVO_4/Sr_2MgSi_2O_7:Eu^{2+}Dy^{3+}$ Heterojunction for Photocatalytic Degradation of Tetracycline and Sustainable Hydrogen Production

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Water and energy are indispensable resources for human life. However, rapid population growth and industrial expansion have led to the contamination of water bodies and the accelerated depletion of fossil fuel resources, which remain the primary energy sources [1,2]. In this context, semiconducting metal oxides are promising catalysts for both the photodegradation of organic pollutants in wastewater and the production of hydrogen (H_2) via water splitting [3]. To develop an efficient material for these processes, $BiVO_4$ emerges as a strong candidate due to its suitable chemical and physical properties, as well as its bandgap energy of approximately 2.6 eV. Combining metal oxides with a persistent luminescent (PeL) material has emerged as a new strategy for producing more efficient photocatalysts. These composites can continue the degradation process after the irradiation has ceased. $Sr_2MgSi_2O_7:Eu^{2+},Dy^{3+}$ (SMSO) is a suitable option, as it exhibits a broad and intense emission centered at 470 nm, long persistence (~20 h), and a high charge storage capacity (10^{15}–10^{16} photons g^{-1}). In this study, the $BiVO_4$/SMSO heterojunction was synthesized via microwave-assisted methods: reflux synthesis for $BiVO_4$ and solid-state synthesis for SMSO. Structural analysis using X-ray diffraction (XRD) and Raman spectroscopy confirmed the formation of monoclinic $BiVO_4$ and tetragonal (melilite) SMSO—both recognized as highly active for photocatalytic applications. Scanning electron microscopy (SEM) images revealed a micrometric elongated cubic morphology for $BiVO_4$, while SMSO did not exhibit a specific morphology. The synthesized system was evaluated for the photocatalytic degradation of tetracycline (TC) under simulated sunlight for 120 minutes. To assess the persistent photoluminescence of SMSO and its effect on the heterojunction, the system was subsequently kept in the dark for an additional 120 minutes. Hydrogen photogeneration was also tested under visible light irradiation for 4 hours. To further investigate the role of SMSO photoluminescence in charge separation and its ability to sustain hydrogen production, the system was monitored for an additional 4 hours in the dark. The photocatalytic degradation of TC achieved approximately 80% efficiency, while hydrogen generation yielded around 150 µmol h^{-1} g^{-1}, maintaining activity even after the light source was turned off. These findings highlight the potential of the $BiVO_4$/SMSO heterojunction for the degradation of organic pollutants and the production of sustainable energy.

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The authors gratefully acknowledge support from UFABC, PPG-CTQ (UFABC), CAPES (Finance code: 0001), FAPESP (grants # 2024/18336-0 and 2023/06812-9, LNNano (grants # 20243303 and 20233304) and CEM-UFABC.

P-45

Solar photoreactor photocatalytic/adsorbents composites

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Innovation in advanced oxidation process technologies is based on the direct use of solar radiation for photochemical conversion applications, with particular emphasis on the treatment of micropollutants in water. This process relies on the production of radical species capable of degrading organic matter and micropollutants present in small quantities in water. Solar photo-oxidation makes it possible to develop an autonomous and ecologically compatible process using solar radiation as the main energy source, making processes more sustainable, less costly and less energy- intensive. Nevertheless, the fluctuations and intermittency of the solar resource affect its performance and processing capacity. Indeed, solar energy is subject to seasonal cycles and diurnal/nocturnal variations, geographical disparities.

In this research project, the aim is to develop a bifunctional adsorbent/photocatalyst composite as a promising solution to overcome the limitations inherent in the use of solar energy. Zinc oxide (ZnO) was combined with activated carbon (AC), which provides a means of storage during phases of low sunlight conditions and facilitates the concentration of micropollutants on the catalyst surface, thus increasing the chances of contact with photo-generated charges (Fig.1).

First, three types of activated carbon were selected to assess their respective sorption efficiencies, this evaluation allowed for the accurate determination of the activated carbon with the best adsorption properties. The adsorption experiments showed that the kinetics followed a pseudo-second-order model, and the adsorption isotherms were well fitted using Langmuir isotherm theory. Thus, Norit-AC is the most appropriate material to be combined with ZnO in a complementary composite. The kinetic constant k_{utile} was found to be $0{,}8\times10^{-3}$ g/mg·min, and the sorption capacity, determined from Langmuir parameters, had a q_{max} value of 121,95 mg.g^{-1}.

Second, in this part, three key functionalities are analyzed in order to optimize the performance of AC/ZnO composites developed: optical properties using a transmittance measurement bench mainly in the ultraviolet range aimed at maximizing the use of light energy; sorption capacity, assessing pollutant storage as well as adsorption/desorption kinetics; and photodegradation efficiency, determining the material's ability to effectively break down contaminants under irradiation. The feasibility of the AC/ZnO composite preparation approach was validated by controlling the AC amount from 1 to 30 % in order to investigate the effect of composition. The results obtained using phenol as a target pollutant molecule, revealed that the prepared materials exhibit both sorption and photocatalytic properties which vary with the AC/ZnO composition. The photodegradation efficiency was close to that of unmodified ZnO, while the composite's adsorption capacity was comparable to that of Norit as a reference. This was followed by an evaluation of their photodegradation performance, emphasizing their high sorption capacity.

This part allowed us to show the adaptability of the AC/ZnO preparation for a wide range of water treatment applications. The functional properties of these materials - which are essential to know in order to consider their integration within a photoreactor - have been determined by a theoretical approach coupled with experimental measurements.

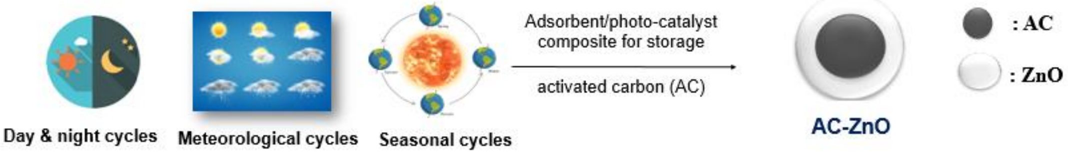

Fig. 1. Fluctuating and intermittent resources.

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Acknowledgements
This work has received financial support from the PHC-Utique project.

P-46

Optimizing CO_2 Photocatalytic Reduction: The Role of Carbon Species Equilibrium in TiO_2 Slurries

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One of the major challenges in contemporary society is energy production, accompanied by the annual emission of 31.5 billion tons of CO_2 from fossil fuel combustion, a primary greenhouse gas [1]. Photocatalytic CO_2 reduction emerges as a promising strategy for mitigating these emissions, as it solely relies on solar radiation [2]. However, this process remains inefficient due to the complexity of photophysical and photochemical reactions involved. The desired products, methane and methanol, require more electrons than by-products such as carbon monoxide, formaldehyde, and formic acid. Additionally, water splitting competes for electrons in reductive environments, leading to hydrogen formation which is particularly attractive as a clean and sustainable energy carrier [3].

The dissolved CO_2 species play a crucial role in photocatalytic reduction [4]. CO_2 exists in equilibrium with bicarbonate and carbonate, with its concentration governed by pH. This study investigates the influence of carbon species equilibrium on product yields in a TiO_2 suspension system under UV irradiation. The goal is to identify optimal conditions for CO_2 photocatalytic reduction.

Experiments were conducted in a stirred batch photoreactor (174 mL) containing a 1 g L^{-1} TiO_2 (P25) suspension, illuminated by an 8 W Hg lamp (λ = 254 nm). The photocatalyst was suspended in NaOH or $NaHCO_3$ solutions with a concentration of 0.2 M. CO_2 or He was bubbled into the suspension for 25 min before irradiation, ensuring saturation and air removal. The reactor was sealed at 120 kPa, and gas samples were analysed using gas chromatography with a barrier discharge ionization detector (BID). pH measurements were done before and after saturation, and total dissolved inorganic carbon (DIC) was quantified via TOC (Total Organic Carbon) analysis.

The results indicate that $NaHCO_3$ solutions saturated with CO_2 produce the highest yields of CO, CH_4, and H_2. Upon CO_2 saturation, both the $NaHCO_3$ and NaOH systems stabilize at pH 6.7, with the carbonaceous species equilibrium comprising approximately 38% dissolved CO_2 and 62% $NaHCO_3$. The enhanced yield correlates with higher DIC availability from both $NaHCO_3$ and CO_2 capture. In contrast, $NaHCO_3$ solutions saturated with He result in higher pH (7.9) and contain only 2% dissolved CO_2, leading to lower yields.

In conclusion, increasing total dissolved inorganic carbon via CO_2 saturated $NaHCO_3$ solutions and favouring carbonaceous species in equilibrium at lower pH significantly enhances the efficiency of photocatalytic CO_2 reduction. This is attributed to the elevated concentration of dissolved CO_2, the key reactant for TiO_2-mediated photoreduction under UV light.

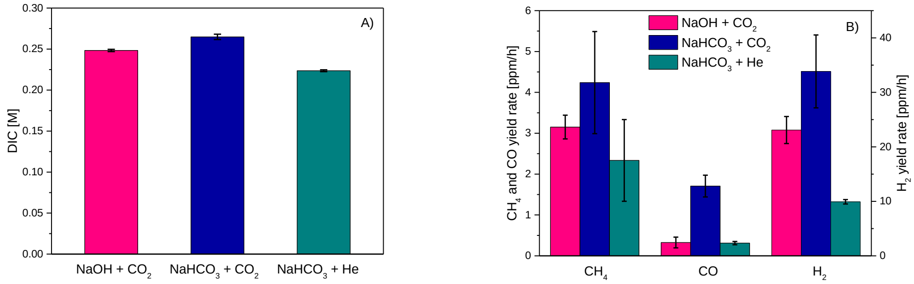

Fig. 1. A) DIC concentration after gas saturation and B) Products yields rate varying the carbon source dissolved in the photocatalyst suspension.

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This work has been produced with the financial support of the European Union under the REFRESH - Research Excellence For REgion Sustainability and High-tech Industries project No. CZ.10.03.01/00/22_003/0000048 via the Operational Programme Just Transition. Experimental results were obtained by using large research infrastructure ENREGAT supported by MŠMT, project no. LM2023056.

P-47

Immobilized Photocatalytic Nanocomposites for Pharmaceutical Wastewater Treatment

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The immobilization of photocatalysts onto stable, reusable supports is crucial for advancing wastewater treatment technologies, particularly in addressing pharmaceutical contaminants. In this study, we develop and evaluate a novel nanocomposite-based photocatalytic system, where silver-phosphate nanodiscs and iron oxide nanoparticles [1, 2] are integrated with carbon nanotubes/cellulose fibre onto flexible ceramic paper. The ceramic paper support ensures mechanical stability, reusability, and efficient photocatalyst immobilization, preventing particle loss and secondary contamination. The photocatalytic efficiency of the immobilized nanocomposite was assessed under visible light irradiation for the degradation of pharmaceutical pollutants. Compared to conventional slurry-based photocatalysts, this immobilized system enables continuous operation in pilot-scale applications with minimal catalyst leaching. Using ceramic paper as a support material enhances durability, while alternative substrates, including polymer membranes and fibrous materials, are being explored for further optimization. Additionally, the incorporation of iron oxide nanoparticles facilitates magnetic separation, offering an efficient recovery strategy. These findings highlight the potential of immobilized photocatalytic nanocomposites for sustainable pharmaceutical wastewater treatment. Future work will focus on optimizing support material properties, improving photocatalyst adhesion, and evaluating system performance under real wastewater conditions in a pilot plant setup.

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The authors are thankful for the financial support from NRDIO Hungary 2021-1.2.6-TÉT-IPARI-MA-2022-00003.
SUPPORTED BY THE UNIVERSITY RESEARCH SCHOLARSHIP PROGRAM OF THE MINISTRY FOR CULTURE AND INNOVATION FROM THE SOURCE OF THE NATIONAL RESEARCH, DEVELOPMENT AND INNOVATION FUND EKÖP-24-3-II-16.

P-48

Photocatalytic activity of various BBN-decorated titania composites

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Basic bismuth nitrate (BBN) is relatively new yet very promising material in the group of photocatalysts, however, there are not many reliable studies on its detailed properties [1]. It is well known that Z-scheme hetero-structured photocatalysts can provide the dual advantage of a wide range of light absorption and strong redox capability [2]. Therefore, the present study aims at combining the new BBN with different forms of titania, which are well recognized to be photocatalytically highly efficient.

To achieve composite materials, the "classical" P25, pure rutile, pure anatase, and natural ilmenite (iron titanate) were applied in the subsequent hydrothermal procedure using relatively low reaction time and temperature (8h, 120°C). To enlighten both the structure and the morphology of as-prepared materials, XRD, SEM, TEM, N_2-adsorption, and DRS were applied for physico-chemical characterization.

The photocatalytic efficiency of the prepared samples was evaluated in a custom-built photoreactor by measuring the degradation rates of two organic pollutants under UV and visible light illumination: the organic dye Plasmocorinth B and the pharmaceutical ibuprofen. The pollutant concentrations were monitored using a UV-Vis spectrophotometer for the organic dye and high-performance liquid chromatography (HPLC) for the pharmaceutical. Among all the samples, **TiO_2-BBN** demonstrated the highest photocatalytic activity, surpassing that of standard P25 when degrading ibuprofen. Complete degradation was achieved in just 20 minutes under UV illumination and 30 minutes under visible light. These results indicate that modifying TiO_2 with BBN enhances its photocatalytic activity under visible light.

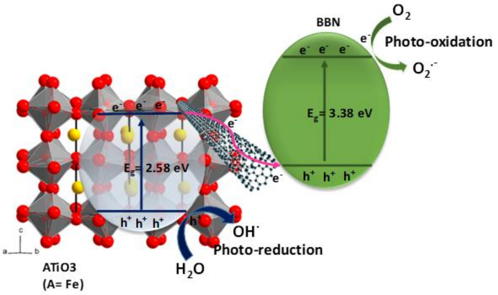

Fig. 1. Schematic model for the photocatalytic composite.

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Acknowledgements

The Authors are thankful for the financial support from NRDIO Hungary (SNN 143949) and ARIS Slovenia (N2-0310).
SUPPORTED BY THE UNIVERSITY RESEARCH SCHOLARSHIP PROGRAM OF THE MINISTRY FOR CULTURE AND INNOVATION FROM THE SOURCE OF THE NATIONAL RESEARCH, DEVELOPMENT AND INNOVATION FUND EKÖP-24-3-II-16.

P-49

Development and testing of immobilized TiO_2 for water treatment: from the lab to pilot scale

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The severe hydric deficit and the inadequate distribution of water resources are crucial problems that require the development of sustainable solutions. The ENERGICA project, funded by the European Commission (GA 101037428), was structured to corroborate the feasibility of applying well-known technologies to overcome problems within the water-food-energy framework in developing countries. In this context, solar-driven immobilized heterogeneous photocatalysis can be applied as a viable tool for simultaneous disinfection and Contaminants of Emerging Concern (CECs) removal from different water matrices since it is an easy-to-operate and environmentally friendly technique for decentralized treatments [1]. The aim of this work is the design, development, and assessment of a solar-photocatalytic prototype coupled with sets of immobilized photocatalysts [2] for simultaneous disinfection and CECs removal in three water matrices of different complexity (isotonic water (IW), well water (WW) and urban wastewater (UWW)).

All the assays were conducted at the facilities of Plataforma Solar de Almería (Almería, Spain). *E. coli* was selected as faecal indicator and quantified by plate counting technique (Limit of detection (LD) = 2 CFU/mL) to assess disinfection efficiency. Additionally, a mix of three CECs (imidacloprid (IMD), sulfamethoxazole (SMX) and trimethoprim (TMP); at 100 µg/L each) was spiked to evaluate decontamination, monitored by Ultra-Performance Liquid Chromatography with an Ultraviolet Diode-Array Detector (UPLC/UV-DAD), following a previously described methodology [3]. Initially, lab scale assays were carried out in 250 mL vessel reactors (Fig. 1a) with different slurry catalysts (1% GO-TiO_2, 5% GO-TiO_2, and P25-TiO_2) at different concentrations (50, 100, 200, 500 and 1000 mg/L). Moreover, the reusability and stability of the immobilized P25-TiO_2 onto a piece of stainless steel (Fig. 1b) was evaluated at lab-scale by the performance of cyclic assays (ten in IW and fourteen in UWW).

The good performance of the stainless-steel piece immobilized with P25-TiO_2 for simultaneous disinfection and decontamination (CECs removal > 80% and the achievement of *E. coli* LD) triggered the scaling-up from lab scale to pilot-scale. A Multi-Step Cascade Reactor (MSCR) was proposed firstly for the treatment of 5 L of water (Fig. 1c), in which assays were carried out with two sets of immobilized steps at different flow rates. The good performance of MSCR_5L motivated the construction of a second prototype for the treatment of 50 L (Fig. 1d), in which the well-known strategy of adding small amounts of H_2O_2 (50 mg/L) enhanced the disinfection rate without remarkable variations in CECs degradation. Further assays are still in progress with other microorganism' target and will be complemented with a LCA study and a techno-economic analysis.

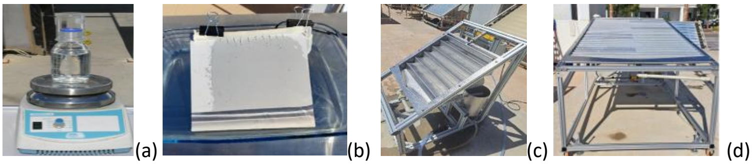

Fig. 1. Lab scale prototypes: solar vessel reactor (a) stainless steel piece coated with TiO_2-P25 (b) Pilot-scale prototypes: MSCR_5L (c) and MSCR_50L (d)

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Acknowledgements

To the financial support from the European Union's Horizon 2020 research and innovation programme under the ENERGICA project (GA 101037428).

P-50

Bipolar anodization as efficient method for synthesis of gradient titania NTs photoelectrocatalyst

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Since 2014, when the first publication about titania nanotubes (TiO_2 NTs) obtained by bipolar anodization was published [1], this topic was only mentioned in less than ten papers. In this process, anodized sample, often called bipolar electrode (BPE), is immersed in electrolyte between driving (feeder) electrodes, and on its two extremities oxidation and reduction reactions are driven by the gradient potential difference (ΔV_{BPE}). Due to this, in contrast to conventional anodization process, bipolar anodization allows to obtain gradient-changing NTs, characterized by different physicochemical and photoelectrocatalytic properties. In this regard, in this work the local characteristic of cylindrical, separated titanium(IV) oxide microstructures depending on its relative position to driving electrodes was examined. Moreover, for full understanding the relation between process parameters as well as TiO_2 NTs morphology and photoelectroactivity, central composite design (CCD) factorial plan was established. Four anodization variables: time, voltage, H_2O content, and sample dimensions were optimized on three different levels. After calcination, each of 26 tests were cut onto 1 cm × 2 cm parts and characterized using UV/Vis spectroscopy, Raman spectroscopy and SEM observations in at least two different points. Photoelectroactivity was determined using IPCE method, showing the relation between applied potential, light wavelength and obtained photocurrent.

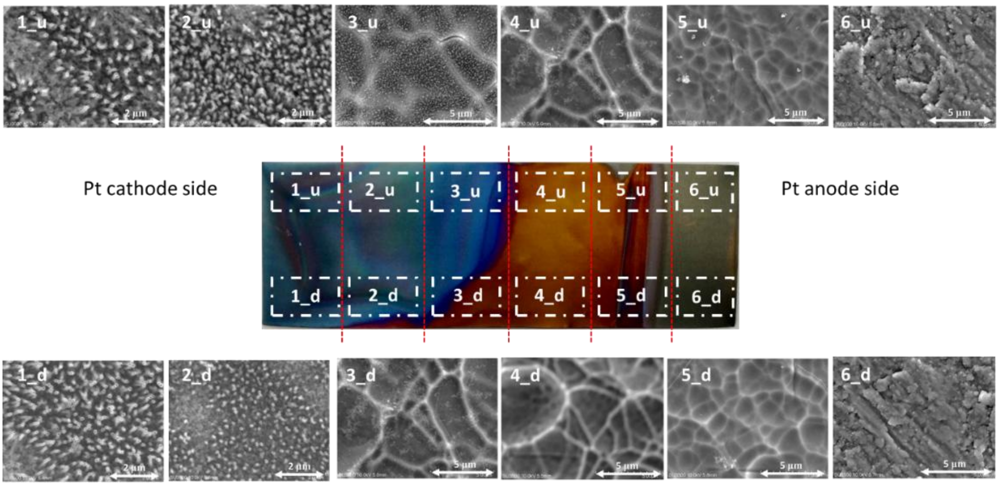

Fig. 1. SEM images captured at different places of the sample anodized according to the bipolar protocol; here: anodization time: 3 h, voltage: 140 V, water content: 10%, the sample dimensions: 2 × 6 cm.

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Acknowledgements

This research has been co-founded by the Polish National Agency for Academic Exchange within Polish Return Program (BPN/PPO/2021/1/00037), the National Science Centre within Miniatura 6 project (2022/06/X/ST5/00321).

Photocatalytic Sand Filters for the Scalable and Continuous Removal of Microplastics from Contaminated Waters

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Microplastic (MP) pollution poses a serious threat to aquatic environments due to the widespread use of plastics and the limited effectiveness of conventional removal methods [1]. This work introduces a novel and scalable solution through the use of a TiO_2-coated silica sand photocatalyst, specifically designed for the effective degradation of MPs and advancement of sustainable water treatment technologies. The material was developed by depositing an optimized TiO_2 layer [2,3] on silica sand and incorporating TiO_2-coated SiO_2 microspheres to enhance the surface. The millimetre-scale size of the sand particles helped to avoid pressure buildup and facilitated separation in continuous flow systems. Structural and optical properties were thoroughly characterized by TEM, FESEM, EDX and UV-Vis diffuse reflectance spectroscopy, while batch experiments were performed to determine the optimal coating thickness. In addition, the chemical synthesis protocol was designed to be reproducible on a larger scale, which would allow for scalable production of the photocatalyst.

A laboratory-scale continuous flow photoreactor was constructed with a glass column illuminated with UV-A LEDs and filled with the scaled photocatalyst, and tested with real wastewater containing PET microplastics (Fig. 1A). Chemical oxygen demand (COD) analysis revealed a 95% reduction in MPs content under UV exposure, confirming efficient degradation driven by the combined photocatalytic activity and the intrinsic filtration capacity of the sand, which promote an increased contact with the pollutants (Fig. 1B). These results demonstrate strong potential for treating water contaminated not only with PET but also with other types of microplastics such as polyethylene and in the presence of additional organic pollutants.

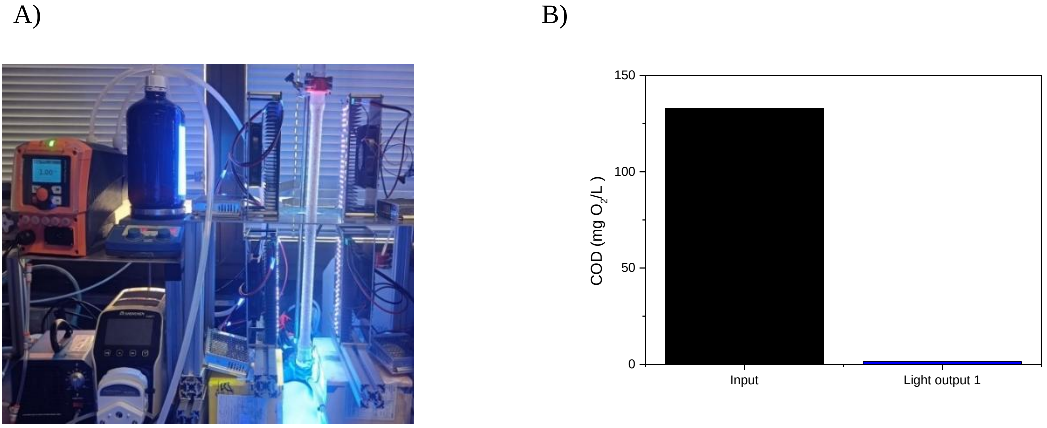

Fig. 1. A) Continuous flow photoreactor. B) COD measurements at the input and outlet under UV-irradiated conditions.

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We gratefully acknowledge the financial support from the Spanish Ministry of Science and Innovation through grants TED2021-131952B-I00 and CEX2021-001230-S (funded by MCIN/AEI/10.13039/501100011033), and the Ayuda a Primeros Proyectos de Investigación (PAID-06-24) from the Vicerrectorado de Investigación of the Universitat Politècnica de València (UPV). We also thank the Generalitat Valenciana and the European Union for co-financing A.B.M. postdoctoral contract (CIAPOS/2023/201) under the European Social Fund Plus Operational Program 2021–2027 (FSE+).

Catalytic Oxidation of Phenol Using Iron-Supported Illite: Optimization of Parameters for Efficient Wastewater Treatment

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This study investigates the catalytic oxidation of phenol using an iron-supported purified natural illite clay catalyst, focusing on optimizing operational parameters and elucidating the degradation mechanism to achieve high efficiency and minimize environmental impact. The effects of pH (2‑10), initial phenol concentration (20‑100 mg/L), temperature (30‑90° C), iron content (3‑7%), catalyst dosage (0.5‑1.5 g/L), and H_2O_2 concentration (4.75‑12 mM) were systematically studied. Optimal conditions were determined at pH 3, a phenol concentration of 50 mg/L, 50° C, 5% iron content, a catalyst dosage of 1 g/L, and 8.7 mM H_2O_2, enhancing hydroxyl radical formation and reaction kinetics. Under these conditions, the catalyst achieved a 99% degradation rate for phenol and an 83% reduction in chemical oxygen demand (COD), with minimal iron leaching. Identification of intermediate by-products using HPLC enabled the construction of a detailed stepwise degradation mechanism, shedding light on the oxidative pathways and confirming the effectiveness of the process. The purified illite catalyst demonstrated excellent stability and reusability over multiple cycles, maintaining performance with minimal activity loss. Comprehensive material characterization (XRD, TGA, BET, SEM, FTIR, and laser granulometry) confirmed the structural and morphological integrity of the catalyst and provided insights into its active sites. This study underscores the potential of iron-impregnated purified natural clays as sustainable, cost-effective catalysts for treating phenolic pollutants in wastewater.

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Charge carriers in CuW$_x$Mo$_{1-x}$O$_4$ and CuW$_x$Mo$_{1-x}$O$_4$/BiVO$_4$ heterojunction system via transient absorption spectroscopy

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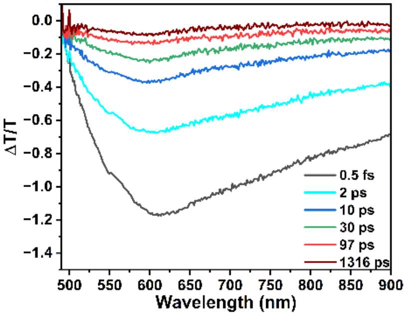
Utilizing most of the solar energy reaching Earth will suffice for our annual energy consumption, and it is a primary goal toward a sustainable and carbon-neutral development [1]. Photoelectrochemical (PEC) water splitting at the semiconductor/electrolyte interface is an efficient way to convert sunlight to clean hydrogen directly, and the interest in this sustainable route is growing constantly [2]. The search for visible light absorbing semiconductors moved from binary oxides (e.g., WO_3 and TiO_2) to ternary oxides (such as $BiVO_4$ and $CuWO_4$), which offer tuneable band structure and band gap energy by changing the metal cations [3]. State-of-the-art $BiVO_4$ photoanodes perform remarkably, but still the overall solar-to-hydrogen (STH) conversion is limited by the 2.4 eV band gap of $BiVO_4$, allowing only an 8 % STH [4]. Copper tungstate ($CuWO_4$), a promising candidate for PEC water oxidation with high stability, has a higher theoretical STH > 10%, but still poor PEC performance. Thus, enhancement by metal substitution (molybdenum for tungsten) and combination with other photocatalysts ($BiVO_4$) can improve charge separation and photocurrent efficiency [5]. In a prior work we studied the PEC performance of $CuW_{1-x}Mo_xO_4$ materials with different Mo for W substitution ($x = 0$–0.8). This study identified the $x= 0.5$ substitution ($CuW_{0.5}Mo_{0.5}O_4$) as the best performing sample exhibiting a 6x higher photocurrent at 1.23 V vs. the reversible hydrogen electrode with respect to pure $CuWO_4$. Intensity modulated photocurrent spectroscopy (IMPS) revealed that the superior PEC performance of $CuW_{0.5}Mo_{0.5}O_4$ relies on the more efficient separation of photoproduced charges compared to $CuWO_4$. We achieved a further enhancement in the 400–480 nm wavelength range by coupling $CuW_{0.5}Mo_{0.5}O_4$ with a $BiVO_4$ overlayer [6]. These results showed that Mo doping in $CuWO_4$ modifies its electronic structure, reducing the bandgap and improving visible-light absorption, and coupling $CuWO_4$ with $BiVO_4$ creates a heterojunction that could promote charge separation and reduce recombination losses.

Fig. 1. TAS spectra of layered $CuWMoO_4$ at 343 nm.



Here, we directed transient absorption spectroscopy (TAS) across femtoseconds to microseconds to probe the charge carrier dynamics in these systems with the aim of better understanding the observed effects. Our up-to-date findings reveal that $CuWMoO_4$ has transient absorption spectral features (Fig. 1) similar to $CuWO_4$. Its charge carriers decay with lifetimes comparable to $CuWO_4$, with a moderate influence due to the film thickness. The combination with $BiVO_4$ in the heterojunction, induces clear changes in the transient spectra and their dynamics which can relate to PEC performance.

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Acknowledgements

This work has received financial support from the Ministero dell'Università e della Ricerca with project 'Charge Transfer Dynamics in Photoactive Materials for Solar Energy Conversion" - CHARM Prot. 20227TKTMY.

Development of Anti-microbial C3N4-ZnO Nanocomposites in Hydrogel coatings for Medical Devices

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Semiconductor photochemistry offers innovative strategies for functionalizing medical device surfaces with antibacterial properties. This study investigates C3N4-ZnO nanocomposites, harnessing their visible-light photocatalytic activity to enhance antibacterial performance. These composites are intended for integration into antifouling hydrogel coatings to improve medical device functionality.

Graphitic carbon nitride (g-C3N4) was synthesized via thermal polymerization of urea and melamine (denoted as g-C3N4(U/M)) at 550°C. Zinc acetate was combined with g-C3N4(U/M) in solvents (water, methanol, or ethanol), and ZnO-g-C3N4 nanocomposites with four distinct morphologies—0D nanoparticles, 1D nanorods, 2D nanosheets, and 3D nanoflowers—were prepared by tuning pH, hydrothermal reaction conditions in an autoclave, and calcination at 350°C for 4 hours in a muffle furnace. Their structure and morphology were characterized using scanning electron microscopy (SEM). Photocatalytic performance was evaluated by measuring the degradation of methylene blue (1 g/L) under LED strips (λ = 440 nm), with reaction kinetics monitored via UV-Vis absorbance at 665 nm.

SEM analysis confirmed the successful deposition of ZnO with diverse morphologies onto g-C3N4(U/M) surfaces. Among the C3N4-ZnO variants, the 0D nanoparticle morphology demonstrated the highest photocatalytic degradation efficiency (84.7% in 60 minutes and 92.8% in 180 minutes under visible light), attributed to enhanced surface area and improved charge separation, outperforming other morphologies. Antibacterial testing is currently in progress.

These findings highlight the potential of C3N4-ZnO nanocomposites as multifunctional materials, paving the way for medical surfaces with superior visible-light photocatalytic and antibacterial performance. Incorporating these composites into antifouling hydrogel coatings could further enhance their applicability in medical settings. Future efforts will focus on optimizing antibacterial properties and developing practical composite coatings.

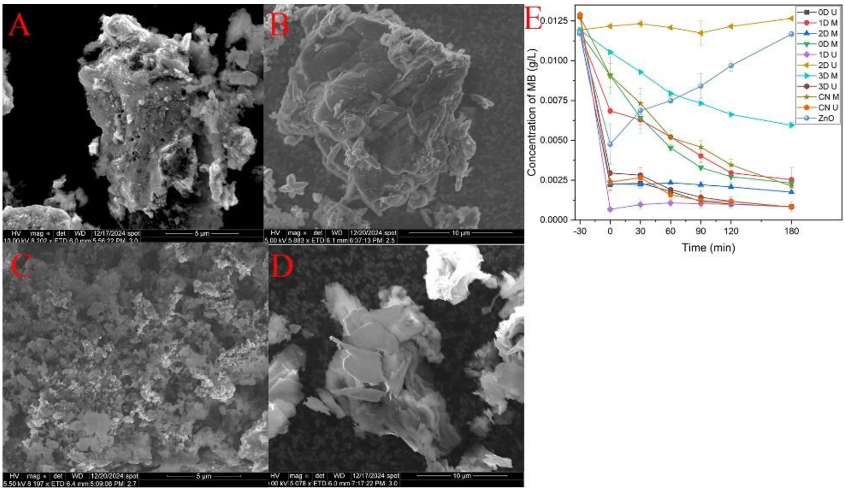

Fig. 1. A-D) SEM images of C3N4-ZnO (0D, 1D, 3D, 2D). E) The degradation of methylene blue with all samples.

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P-55

$CaMn_{1-x}FexO_3$ Perovskites as Catalysts for the Photosensitised Oxygen Evolution

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The oxygen evolution step is still one of the bottlenecks of an artificial photosynthetic systems. To overcome these limitations, catalysts of a variety of compositions have been investigated for photo-induced water oxidation. However, designing catalysts that are robust, efficient, and, at the same time, composed of elements that are non-toxic and widely available on the Earth's crust remains as a major challenge. Taking inspiration from the active site of Photosystem II which consist of an inorganic catalytic core of the cluster Mn_4CaO_5, in this work we have explored the performance of $CaMn_{1-x}Fe_xO_{3-\delta}$ perovskites, which also presents Ca-O-Mn moieties for the photoassisted oxygen evolution reaction. Accordingly, we expect these fully inorganic materials based on abundant elements can act as an effective photocatalysts for this process

Perovskites with two different compositions, $CaMnO_3$ and $CaMn_{0.7}Fe_{0.3}O_{3-\delta}$, were prepared using Pechini method and XRD analyses confirmed the formation of a single phase with $GdFeO_3$-type orthorhombic structure. XPS of these samples reveals that redox metals are mainly present as Fe^{3+} and Mn^{4+} and in accordance with electroneutrality of the lattice, a larger concentration of oxygen vacancies is expected for the Fe-doped perovskite.

Both perovskites act as effective catalysts for water oxidation, producing O_2 in the presence of $[Ru(bpy)_3]^{2+,}$ as photosensitizer and $Na_2S_2O_8$ as a sacrificial agent. However, Fe-doping of the $CaMnO_3$ oxide significatively promotes photocatalytic activity [1]. Remarkably, not only oxygen production declines only very slightly after five consecutive cycles, but $CaMn_{0.7}Fe_{0.3}O_{3-\delta}$ remains stable under these conditions, without any noticeable changes, thus making it a convenient reusable photocatalyst.

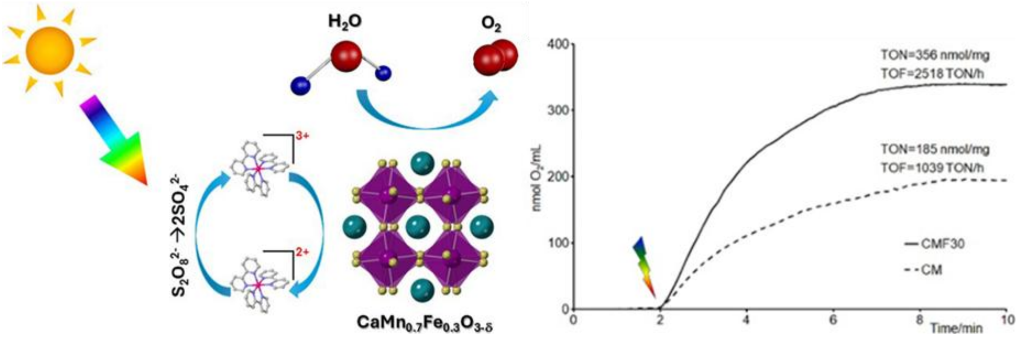

Fig. 1. Scheme showing the basic mechanism of the photosensitised oxygen evolution, together with the time variation of the production of O_2 upon illumination over $CaMnO_3$ and $CaMn_{0.7}Fe_{0.3}O_{3-\delta}$

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Acknowledgements

This work has received financial support from the by the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 746167, the Italian Ministry of Foreign Affairs and International Cooperation (PGR project on Artificial Photosynthesis, collaboration Italy-Japan, Grant Number JP21GR09) and by the European Union (NextGeneration EU), through the MUR-PNRR project SAMOTHRACE (ECS00000022).

Construction of novel MoS_2/BiOX (X = Cl, Br, I) heterojunctions with an enhanced photocatalytic activity for pollutants degradation

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For decades, global environmental pollution and energy shortage are major concerns of mankind and have attracted extensive attention. To tackle these issues, a lot of efforts have been made to develop efficient semiconductor photocatalysts. So far, it has been revealed that semiconductor materials, such as MoS_2, exhibit high photocatalytic activities, especially in H_2 production. However, MoS_2 shows poor photocatalytic efficiency for the utilization of visible light due to its high recombination rate of photo-generated electrons and holes. Being highly stable and active, the low-cost and non-toxic BiOX has attracted widespread attention recently. The layered BiOX semiconductors belong to the PbFCl-type tetragonal crystal system bearing a P4/nmm space group, which is built by [Bi_2O_2] slabs and slabs of double halogen atoms along the z-axis direction. Several strategies have been developed to enhance the photocatalytic behaviour and promote the separation of photogenerated electrons-holes in bismuth-based photocatalysts, including ion doping, assembling heterojunctions, controlling morphology with modifiers or creating oxygen vacancies. Especially, the formation of heterojunctions by coupling semiconductors has demonstrated to be a successful strategy for enhancing the photocatalytic performance of individual semiconductors. This strategy promotes electron-hole separation while intensifying the internal electrostatic field. Thus, the photocatalytic ability of a heterojunction depends on factors such as the intimate contact of the semiconductors and their energy band positions [1,2].

Here, we fabricated MoS_2/BiOX (X = Cl, Br, I) composites (Fig. 1) by a facile one-step hydrothermal approach, and the products showed the improved efficiency of electron-hole separation across the MoS_2/BiOX heterojunction for the photocatalytic degradation of several pollutants, such us dyes (Rhodamine B) and herbicides (Acetamiprid).

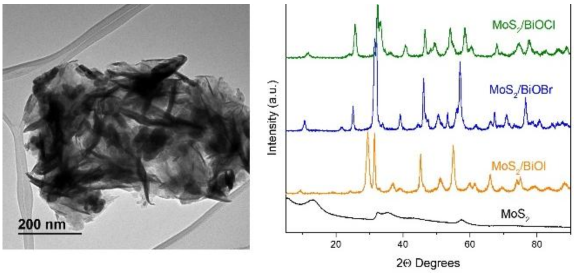

Fig. 1. *TEM image and XRD patterns of MoS_2/BiOX composites.*

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Acknowledgements

Authors thank the projects titled “Materiales semiconductores con aplicación en fotoelectrocatálisis: Desarrollo de sistemas sinérgicos para la degradación de contaminantes y producción de H_2 y/o O_2” and "Heterouniones 2D de Vanadatos y Titanatos Aplicadas en la Degradación de Contaminantes y la Producción Simultánea de H_2 Verde vía Fotoelectrocatálisis" funded by Universidad Rey Juan Carlos, and the project “Agentes generadores de ROS basados en materiales nanoestructurados multifuncionales para aplicaciones ambientales y terapéuticas” (PID2022-136417NB-I00) funded by MICIU/AEI /10.13039/501100011033 and FEDER, UE.

Simultaneous degradation of pollutants and H_2 production with photoelectrocatatalysis using 2D/2D TiO_2-$BiVO_4$ heterojunctions

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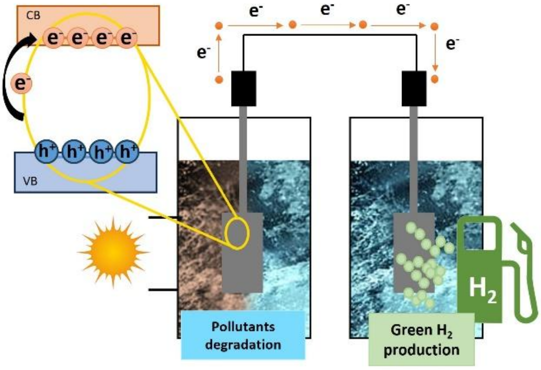
The energy and environmental crisis that society currently faces makes it necessary to seek sustainable alternatives to traditional energy sources. In this context, "green hydrogen" emerges as a proposal against climate change, and in this direction, water splitting methods present themselves as an alternative to other traditional methods of obtaining H_2. For these methods to be environmentally sustainable, responsible management of the natural resources required for their production is crucial, which is especially important in recent times in the case of water, due to its scarcity and associated pollution problems. Photoelectrocatalysis emerges as a promising advanced electrochemical oxidation process by combining both photocatalytic and electrolytic processes that allow simultaneous hydrogen production and water decontamination (Scheme 1).



Scheme 1. *Schematized photoelectrocatalytic process.*

In this regard, in the search for new materials for the preparation of effective photoanodes in photoelectrocatalytic reactions, two-dimensional (2D) materials are attracting increasing attention due to their unique properties that are being widely investigated. Among the most commonly used layered semiconductors as photoanodes, bismuth vanadates ($BiVO_4$) stand out for their high photoelectrochemical stability in aqueous media and their reduced band gap. However, they exhibit poor electronic mobility due to the rapid recombination of electrons in the valence band, so the design of heterojunctions has proven to be an effective strategy to overcome the deficiencies of these processes, as they improve the movement of charge carriers in the system. In this work, heterojunctions based on $BiVO_4$ and 2D-TiO_2 doped with **metals** have been prepared and their use as photoanodes in the photoelectrocatalytic reaction **of some pollutant's** degradation and simultaneous H_2 production has been studied. For this purpose, both the preparation of the electrode (type of deposition, carbonaceous material, conductive support, etc.) and the reaction conditions (solvent, acetamiprid concentration, and other parameters) have been optimized.

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Acknowledgements

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Printable Photocatalytic Coatings Based on Graphitic Carbon Nitride and Poly(heptazine imide): A Brick-and-Mortar Approach

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Photocatalytic coatings represent a promising avenue for developing functional surfaces capable of harnessing light energy for environmental remediation and chemical transformations. Among various photocatalytic materials, graphitic carbon nitride (g-C_3N_4, GCN) stands out due to its suitable band gap for visible-light absorption, chemical stability, and low-cost synthesis. However, challenges remain in integrating GCN into robust, scalable, and patternable coating architectures suitable for real-world applications. In this work, we present a hybrid coating formulation consisting of exfoliated GCN flakes and a colloidal dispersion of poly(heptazine imide) (PHI).

The GCN flakes used in this work were synthesized through a supramolecular precursor strategy involving melamine and cyanuric acid. The supramolecular complex was isolated, dried, and subsequently thermally treated under nitrogen atmosphere to yield bulk GCN. To enhance the film-forming ability and improve dispersibility, the resulting GCN was wet-milled in propan-2-ol using a custom ball-milling setup with glass beads, producing a stable 10 wt% colloidal dispersion. This exfoliated form, characterized by reduced particle size and improved monodispersity, was directly employed in the coating formulations. The methodology builds upon our prior work [1] and draws inspiration from the supramolecular assembly approach introduced by Lotsch and colleagues [2].

To formulate the printable coating mixture, the GCN flakes were combined with a colloidal dispersion of poly(heptazine imide) (PHI), which serves as a semisoluble binder. The PHI was synthesized using an ionothermal method adapted from Savateev and co-workers [3]. This approach yields water-processable PHI colloids that exhibit stability, mild photoactivity, and strong film-forming capabilities. Their inclusion in the formulation not only promotes adhesion of GCN flakes to substrates but also enhances the mechanical robustness and uniformity of the resulting coatings, crucial for reproducible screen printing and long-term photocatalytic performance.

This hybrid coating strategy adopts a “brick-and-mortar” architecture, wherein exfoliated GCN flakes act as the photoactive “bricks” and the PHI binder functions as the “mortar” that interconnects and stabilizes the particulate network. This design not only enhances the mechanical integrity of the coating but also ensures intimate contact between the photocatalytic domains and the substrate, which is essential for efficient light-driven processes. Such an approach has proven effective in other fields of materials science, particularly in the development of functional films and electrodes [4,5], and is now innovatively applied here for the fabrication of photocatalytic layers. The resulting composite structure offers a balance between photoactivity, structural cohesion, and processability, making it ideal for scalable applications using techniques like screen printing.

A key advantage of the proposed formulation lies in the tunable rheology of the coating mixture, which can be adjusted over a wide viscosity range by modulating the PHI–solvent interactions. As described in reference [3], PHI colloids exhibit a quasi sol–gel transition behavior, allowing the formulation to transition between low-viscosity dispersions and gel-like states depending on solvent composition, concentration, and ionic strength. This property enables precise control over the flow, leveling, and film formation characteristics of the coating, making it exceptionally well-suited for screen printing. Moreover, this rheological flexibility opens opportunities for adapting the same formulation to other patterning techniques, such as doctor blading, inkjet printing, or spray deposition, thereby broadening the application landscape for GCN–PHI photocatalytic coatings.

In the upcoming presentation, we will showcase the application of this hybrid formulation in the fabrication of photoanodes via screen printing onto fluorine-doped tin oxide (FTO) substrates. By systematically varying the coating thickness—controlled through screen mesh size and the number of printed layers—and applying post-printing thermal curing, we investigate the influence of these parameters on the resulting photocurrent densities. This allows us to assess how the structural and interfacial properties of the GCN–PHI layers affect their photoelectrochemical performance. These findings will provide insight into the optimization of printable photocatalytic systems and highlight the potential of this formulation for scalable, patterned photoelectrode development.

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Acknowledgements

This work has received financial support from the Czech Science Foundation through project 23-06843S.

Broad-Spectrum Photocatalytic Removal of Indoor Formaldehyde and Acetaldehyde Using Biochar-TiO_2 (P25) Hybrid Under UV and Dual Visible-Light Irradiation (405 & 450 nm)

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Indoor air quality has become a critical public concern in recent decades because people spend nearly 90% of their time indoors, where pollutants can often exceed outdoor levels [1]. Among the various indoor pollutants, formaldehyde and acetaldehyde are widely recognised as two of the most essential aldehydes due to their broad environmental presence and well-documented health risks, justifying their prioritisation in air quality monitoring and health risk assessments. [2]. Both are ubiquitous volatile organic compounds (VOCs) emitted from wood and potentially surpass the health guidelines. [3]. Subsequently, emission of formaldehyde and acetaldehyde from wood is mainly due to the thermal and chemical breakdown of wood polymers, with emissions further influenced by wood species, moisture, temperature, and processing methods [4], [5]. Engineered wood products and certain adhesives can greatly amplify these emissions.

Photocatalysis has emerged as a promising green alternative because it can degrade VOCs under light irradiation and mineralise them into harmless end products such as CO_2 and H_2O without generating significant secondary waste [6]. Titanium Dioxide (TiO_2, particularly P25) is the main benchmark of photocatalyst due to its strong oxidative power, photostability, abundance, and low cost. However, TiO_2 is mainly active under ultraviolet light, which accounts for only 5% of solar spectrum, limiting its practical on indoor application. To overcome this limitation, coupling TiO_2 with carbonaceous materials such as biochar offers several advantages. Biochar not only enhances pollutant adsorption and electron transfer but can also extend light absorption into the visible region. The development of biochar–TiO_2 hybrid photocatalysts has thus attracted increasing interest for indoor air remediation. Furthermore, exploring their activity under broad-spectrum irradiation, including both UV and dual visible-light wavelengths (405 and 450 nm), is essential to evaluate their real potential for practical indoor applications.

In this work, a Biochar–TiO_2 hybrid with several different ratios was tested for the adsorption and photocatalytic degradation of formaldehyde and acetaldehyde under broad-spectrum conditions, including UV and dual visible-light wavelengths (405 and 450 nm), to mimic realistic indoor irradiation. The performance of the hybrid was systematically evaluated using an FTIR spectrometer equipped with mass flow controllers to precisely regulate the supply of air and contaminants, ensuring controlled and reproducible testing conditions. Adsorption experiments were carried out under dynamic conditions to assess the capacity of pollutant uptake, whereas photocatalytic degradation was investigated under steady-state conditions to ensure reliable quantification of the light-driven reactions. The hybrid exhibited higher removal efficiency toward formaldehyde than acetaldehyde, with values of 87.5%, 69 %, and 31% under UV-A lamps and visible light irradiation at 405 and 450 nm, respectively, while acetaldehyde removal efficiencies were 79%, 27%, and 7% for the Biochar:TiO_2 ratio of 1:9 under the corresponding conditions. Notably, the shift from UV-A to longer visible wavelengths improved energy efficiency, as visible-light LEDs generally provide higher electrical-to-optical conversion efficiency and lower operational costs compared to conventional UV-A lamps. In addition, the target pollutants were found to undergo complete mineralisation, with CO_2 and H_2O detected as the sole end products.

In summary, the Biochar–TiO_2 hybrid shows promise as an energy-efficient photocatalyst, operating effectively from UV-A to visible light up to 450 nm, with higher activity toward formaldehyde and complete mineralisation into CO_2 and H_2O, making it suitable for indoor air purification.

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Facile Preparation of Nanoporous Polyphenylene Oxide /Photocatalyst Composites and Their Photocatalytic Performance

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Water, an indispensable component of life, holds unparalleled value for all living organisms. However, its quality is rapidly deteriorating, posing an escalating global crisis. This degradation is primarily driven by severe water pollution stemming from industrial discharges and the relentless pressure of a burgeoning global population. Among the most significant contributors to this pervasive water contamination are organic pollutants, predominantly originating from the textile and food industries. These industries, through their processes, release a wide array of complex organic compounds into water bodies, profoundly impacting aquatic ecosystems and human health [1]. Water pollution is an escalating global concern, largely driven by industrial expansion and population growth, with organic contaminants from the textile and food industries being among the primary contributors [2]. These problems require the development of cost-effective wastewater treatment techniques. While conventional methods like chemical treatment, adsorption, filtration, and ion exchange are employed, photocatalytic oxidation is gaining significant attention as a promising advanced approach due to its efficiency in degrading persistent organic pollutants. Among the various wastewater treatment techniques, heterogeneous photocatalysis based on semiconductor materials stands out as a highly promising and emerging process for the effective degradation of organic pollutants. This advanced oxidation process (AOP) leverages the power of light source and semiconductor materials to initiate chemical reactions that break down stubborn organic contaminants into less harmful, and often completely mineralized, products. Although heterogeneous photocatalytic nanoparticles are effective for wastewater treatment, their practical application is often limited by difficulties in nanoparticle separation and their tendency to aggregate, which significantly diminishes photocatalytic activity [3]. This study addresses these challenges by anchoring semiconductor nanoparticles onto a lightweight, flexible polymeric support—polyphenylene oxide (PPO)—to form stable, ribbon-like structures via a liquid shear-driven process (Fig. 1). PPO is particularly advantageous due to its ability to form nanocrystalline structures upon sorption and desorption of suitable guest molecules, enabling the controlled integration of nanoparticles within a stable polymer matrix. In this work, the photocatalytic performance of a PPO/Fe-ZnS composite was evaluated for atrazine removal. The composite was synthesized in nanocrystalline form with varying Fe-ZnS loadings (4%, 8%, 12%, and 16%) to assess their effect on the photocatalytic efficiency of the PPO-based composite materials. Experimental results demonstrated that nonporous crystalline PPO/Fe-ZnS with an 8% Fe-ZnS loading exhibited the highest photocatalytic efficiency among all tested compositions, achieving 68% pollutant removal after 180 minutes of UV light irradiation. This enhanced performance may be attributed to the uniform and stable distribution of the catalyst on the PPO support matrix. The presence of a nonporous crystalline (NC) phase is a critical factor in achieving high photocatalytic efficiency. PPO synergizes with the photocatalyst, make it a potential candidate for large-scale water purification via photocatalytic oxidation.

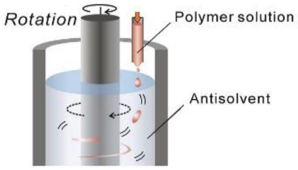

Fig. 1. Schematic of the shear driven process used for composite preparation.

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Photocatalytic upcycling of environmentally relevant PET microplastics for hydrogen generation and value-added chemical synthesis

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Microplastics (MPs), whether intentionally added to products or formed from the breakdown of larger plastics, are an escalating environmental threat. Poor plastic waste management contributes to their spread in ecosystems, where their tiny size, persistence, and ability to carry other pollutants pose serious risks to wildlife and human health. Tackling this challenge requires improved waste management strategies and new technologies to reduce MP pollution. At the same time, transforming MPs into useful products like fuels or chemicals offers a promising "waste-to-value" pathway that supports both clean-up efforts and the circular economy. Photocatalysis is gaining attention as a green, energy-efficient method for breaking down MPs in water. Solar reforming can activate strong C–H and C–C bonds in plastics under mild conditions, offering a sustainable alternative to energy-intensive techniques like pyrolysis. Lately, Lin et al. used g-C_3N_4 supported single-atom Fe catalysts to both degrade MPs and generate H_2. Their system decomposed ultrahigh molecular weight polyethylene (< 5 mm) into oxygenated compounds like carboxylic acids with a 64% selectivity at a 92% degradation rate, and produced H_2 at a 42 $\mu mol \cdot h^{-1}$ rate under simulated sunlight, the activity being driven by hydroxyl radicals through H_2O_2 activation. The study showcased how photocatalysis can jointly tackle plastic pollution and contribute to clean energy production [1-2].

Although progress has been made in upcycling MPs, much of the research falls short of real-world relevance. Most studies rely on uniform, lab-made MPs that fail to reflect the diverse, weathered particles found in the environment. In reality, environmental MPs are typically irregular in shape and size, and undergo chemical alterations by sunlight exposure and physical wear, with a clear impact on how they break [3]. Moreover, many experimental protocols solely focus on the valorization of pretreated plastic-derived products, overlooking the presence of residual MPs that would realistically coexist in the reaction medium. To enhance the relevance of such research, it is crucial to account for these complex, mixed-phase environments, where partially degraded plastics and intermediates coexist, potentially affecting the product distribution and the catalytic performance, factors that are often neglected in current studies. In this study, we explore the photocatalytic degradation and valorization of Polyethylene Terephthalate (PET) MPs (<300 µm) under simulated solar light using a Pt (1 wt.%)/TiO_2-P25 reference catalyst. To better mimic real-world conditions, both commercial PET and environmentally relevant particles prepared via grinding and milling were tested. MPs were first hydrolyzed in 10 M NaOH at 50 °C, and further used to evaluate hydrogen production from both the resulting soluble products and the remaining, partially degraded plastics. This approach enables us to evaluate how mixed plastic fractions affect photocatalytic activity and product selectivity. A continuous-flow quartz reactor coupled with online µGC was used for real-time hydrogen monitoring, while NMR spectroscopy identified the liquid-phase products. As shown in Fig. 1, H_2 was generated in both treated and untreated systems, reaching up to a rate of 4.6 mmol (H_2) g_{cat}^{-1} h^{-1}. This showed the photocatalyst's ability to valorize PET and to produce high added-value chemicals.

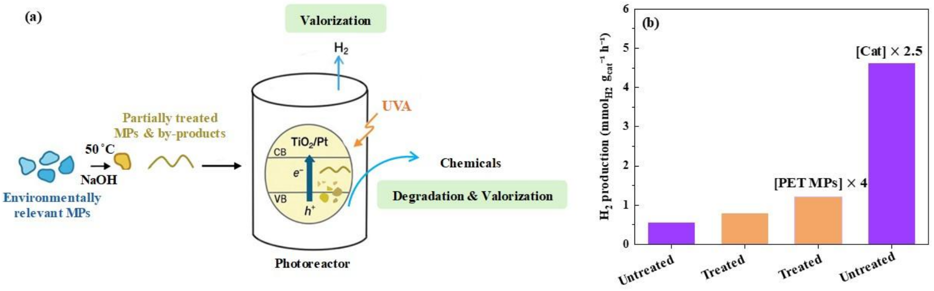

Fig. 1. (a) Schematic figure of PET MP ucycling via solar light photocatalysis. (b) H_2 production over Pt/TiO_2 (1 wt.%) using untreated and pre-treated MP suspensions, tested across varying catalyst content (0.1–0.3 g L^{-1}) and PET load (2.5–10 g L^{-1}).

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Application of biochar-supported lanthanide oxide catalysts in heterogeneous photocatalytic treatment of acetaminophen, diclofenac, and metamizole

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INTRODUCTION

Emerging contaminants (ECs), such as pharmaceutical compounds including acetaminophen (ACE), diclofenac (DCF) and metamizole (MTZ) have garnered increasing attention due to their potential environmental and health hazards [1]. The persistence of these substances at trace levels even after conventional treatment in wastewater treatment plants highlights the urgent need for advanced treatment technologies capable of fully removing them. In this regard, advanced oxidation processes (AOPs) have emerged as promising technologies, with H_2O_2-assisted photocatalysis demonstrating high depuration efficacy against bio-recalcitrant substances [2]. Extensive research has focused on various catalytic materials, notably Fe-based supported photo-catalysts. However, the optimal performance of these systems typically requires acidic pH conditions, which can lead to substantial Fe leaching [3]. Biochar has shown potential to mitigate this issue by stabilizing Fe species through interactions with its surface functional groups, thereby enhancing pollutant degradation. Additionally, substituting Fe with alternative elements may further reduce leaching while improving contaminant removal efficiency [4]. In this study, three catalysts incorporating rare earth elements (namely: Ce, La, and Nd) supported on biochar were synthesized and evaluated in various AOPs for the removal of pharmaceuticals.

MATERIALS AND METHODS

Biochar-supported lanthanide oxides were synthesized via one-step impregnation using Ce, La, and Nd nitrates (0.25 w/w to 105ºC oven-dried pine needles waste). Impregnated biomass was pyrolyzed at 500 °C for 2 hours with a 10 °C/min ramp [5]. Catalysts were characterized using XRD, BET, and SEM analyses. Photocatalytic degradation of $5\ mg\cdot L^1$ ACE, DCF, and MTZ was conducted at circumneutral pH under UVA-LED (385 nm) with or without H_2O_2 stoichiometric dosage. Pollutant degradation, mineralization, H_2O_2 consumption, and metal leaching were monitored using HPLC, TOC, spectrophotometry, and ICP analysis, respectively.

RESULTS AND DISCUSSION

XRD analysis confirmed the formation of CeO_2 on the surface of the Ce biochar-supported catalyst, while the La- and Nd-based catalysts exhibited amorphous structures. BET surface areas were comparable, measured at 22.9 m^2/g for Nd, 12.2 m^2/g for La, and 12.9 m^2/g for Ce-loaded materials. SEM images revealed the presence of cerium oxide nanoparticles on the surface of the Ce-loaded material; but La and Nd were detected, indicating that the formation of the targeted lanthanide oxide phases was not achieved. Neither the La- nor Nd-supported catalysts showed ACE degradation under photocatalytic conditions, with or without H_2O_2. In contrast, the Ce oxide biochar-supported catalyst addressed 80% ACE degradation under UVA-LED H_2O_2-assisted photocatalysis after 2 h, and only 30% was achieved without H_2O_2 dosage. Additionally, this catalyst also addressed ≈70% degradation of DCF after 2h of the same treatment, and MTZ was completely removed within just the first 10 minutes of reaction.

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Acknowledgements

This contribution has been developed in the frame of Project PID2021-124021OB-I00 (URBRAINTREAT), funded by MCIN/AEI/10.13039/501100011033 and "ERDF: A way of making Europe"; and LIFE GreenLED (LIFE22-CCA-NL-101114560), co-funded by the European Union. A.L. Garcia-Costa thanks Comunidad de Madrid for the Cesar Nombela Grant (2023-T1/ECO-29062).

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Application of advanced oxidation processes for pharmaceutical residues elimination in wastewater

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Amisulpride is an antipsychotic drug prescribed to ease the symptoms of schizophrenia. Citalopram is a type of antidepressant used to treat depression and panic attacks. Metoprolol (beta-blocker), candesartan and irbesartan (angiotensin receptor blockers) are applied to treat hypertension and heart failure [1]. All of them are considered as emerging contaminants (ECs) because of their widespread presence in natural environments and their potential to provoke detrimental ecological effects. Wastewater treatment plants (WWTP) have been identified as the main route for ECs to enter water bodies since they are permanently released through treated wastewater (TWW) [2].

Advanced oxidation processes (AOPs) have been widely applied to eliminate organic pollutants in water by the generation and use of strongly oxidizing species, such as hydroxyl radicals ($OH^{\bullet}$), which are highly reactive, non-selective and able to transform harmful compounds into less dangerous products. Among them, heterogeneous photocatalysis and photo-Fenton process have been the subject of great research interest due to their simplicity and higher removal performances. Photocatalysis uses semiconductors as catalysts to produce the $OH^{\bullet}$ radicals. TiO_2 P25 Degussa is one of the most widely tested because of its photochemical stability, commercial availability, non-toxic nature and low cost, high photoactivity and ease of preparation in the laboratory [3]. Fenton process uses ferrous ions (Fe^{2+}) as catalysts and an oxidant to generate $OH^{\bullet}$ radicals. If mediated by UV radiation, Fe^{2+} is regenerated through the reaction between produced ferric ions (Fe^{3+}) and the oxidant, forming more radicals. But this process is strongly dependant to acidic conditions (pH≈3), which implies additional costs for acidification and later neutralization. The use of ligands, such as nitrilotriacetic acid (NTA) or ethylenediamine-N,N'-disuccinic acid (EDDS), as chemical additives can solve this problem by forming stabler complexes with iron ions at natural pH [4]. In this work we have assessed and compared the effectiveness of TiO_2 photocatalytic process and Fenton-like process at neutral pH, using $Na_2S_2O_8$ as oxidant and solar irradiation, for the decontamination of wastewater polluted with residues of five drugs (amisulpride, citalopram, metoprolol, candesartan and irbesartan).

Experiments were carried out with biologically purified water (secondary treatment) collected from a modular WWTP (AT-8) from Augustspain (Spain). Five hundred mL of water spiked at 200 µg L^{-1} were introduced in pyrex glass vessels and maintained in continuous agitation. After adding the corresponding reagents, the vessels were exposed to solar irradiation during 240 min. Five treatments were assayed: i) addition of TiO_2 and $Na_2S_2O_8$, ii) addition of Fe^{3+}:EDDS (1:1) and $Na_2S_2O_8$, iii) addition of Fe^{3+}:NTA (1:1) and $Na_2S_2O_8$, iv) addition of $Na_2S_2O_8$, and v) without reagent addition. Water samples were taken at scheduled times and later analyzed by LC-MS^2 following the procedure described by Fenoll et al. [5]. Results showed that photocatalytic process with TiO_2 and $Na_2S_2O_8$ is the most efficient treatment for compounds removal, with degradation percentages varying from 57.1 to 99.4 % (for citalopram and candesartan, respectively). Regarding Fenton-like treatments, degradation efficiencies ranged from 35.6 to 91.1 % for Fe^{3+}:EDDS complex (for citalopram and candesartan, respectively) and 22.0 to 83.3 % when Fe^{3+}:NTA was utilized (for citalopram and candesartan, respectively). Finally, in treatments conducted without catalyst, degradations ranged from 18.4 to 75.2 % for only oxidant addition and from 1.8 to 25.8 % for photolysis (for citalopram and candesartan, respectively).

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This study formed part of the AGROALNEXT programme and was supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1) and by Fundación Séneca with funding from Comunidad Autónoma Región de Murcia (CARM).

Remediation of strobilurin pesticide-polluted soils by solar photocatalytic treatment

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Despite the fact that the occurrence of pesticides in agricultural soils is a growing environmental problem, the application of agrochemicals is still a commonly used practice to combat pests and diseases throughout the cultivation cycle. Although chemical substances that are currently available on the market are less harmful, their toxic nature still requires strategies for farm soil remediation to mitigate contamination and to further protect consumers. In this sense, Advanced Oxidation Processes (AOPs) comprise a group of techniques able to destroy organic pollutants on site thanks to the generation of strong oxidizing species, like hydroxyl radicals ($OH^\bullet$). In particular, photocatalytic oxidation using semiconductor oxides is an area of environmental interest for the treatment of polluted soil. Among the photocatalysts studied, TiO_2 stands out because of its photo-stability, inert nature, low cost, availability and capability to adsorb reactants under efficient light activation [1]. The objective of this study was to evaluate the effectivity of TiO_2 photocatalysis under solar irradiation in the degradation of four strobilurin compounds (azoxystrobin, kresoxim methyl, pyraclostrobin and trifloxystrobin) in two different agricultural soil matrices.

Soil A was collected from an agricultural area of Region of Murcia (SE Spain). Then, this soil was modified by adding manure as organic amendment to produce soil B. Both soils were spiked with active ingredients of strobilurin compounds to reach an individual level of 1000 µg kg^{-1}. Experiments were conducted introducing 30 g of polluted soil in Petri plates (90 × 15 mm) and adding the corresponding amounts of catalyst (TiO_2 Degussa P25) and deionized water. Then, samples were exposed to sunlight from 9 a.m. to 4 p.m on different days. Three treatments were assayed: (i) TiO_2 addition and sunlight exposure (photocatalytic treatment), (ii) catalyst-free soils but with sunlight exposure (photolysis), and (iii) without catalyst addition nor sunlight exposure (darkness). Soil moisture content was controlled daily and kept constant during the photoperiod. Soil samples were collected in triplicates at 0, 6, 12, 24 hours of accumulated solar irradiation. Pesticide residues isolation from soil was carried out following the procedure reported by Fenoll et al. [2]. Samples were later analyzed by liquid chromatography with tandem mass spectrometry using a triple quadrupole in selected reaction monitoring mode (LC/MS^2). Figure 1 represents the degradation rate constants, estimated according to first-order decay model, obtained for strobilurin pesticides during the different treatments in both soils. As can be seen, a notorious increase in degradation rates was observed in all cases for the process performed with TiO_2. It was also observed a clear influence of soil characteristics in pesticides removal, as indicates the greater rates observed for soil A (the soil with lesser organic matter content). This can be explained by organic matter activity as $OH^\bullet$ scavenger and its capacity to react with OH radicals faster than soil pollutants [3].

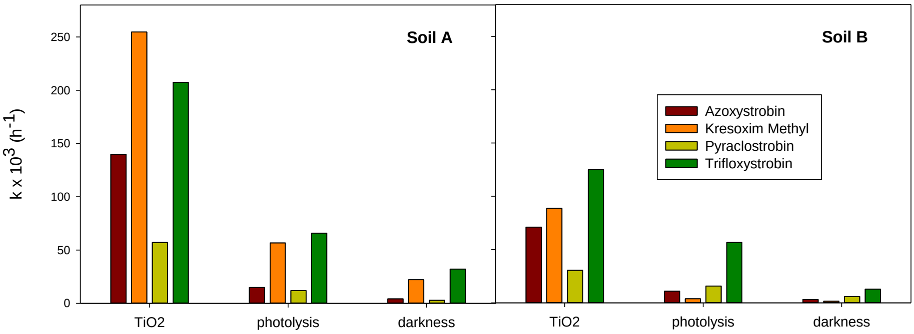

Fig. 1. Strobilurin degradation rate constants obtained for the different treatments assayed in the two soils tested.

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The authors thank the financial support received by the Project PID2022-143118OR-I00 from the Ministerio de Ciencia e Innovación. The authors are also grateful to H. Jiménez, J. Cava, I. Garrido, C. Colomer, M.V. Molina and E. Molina for technical support.

Simultaneous Removal of *Enterococcus* faecalis and Tetracycline from Wastewater Using the PMS/N-doped Biochar/Solar Process.

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Efficient removal of microorganisms and contaminants of emerging concern (CEC, e.g. antibiotics) from wastewater remains a major environmental challenge [1], [2]. As antibiotics enter the environment, microbial communities can be harmed, and antibiotic-resistant bacteria may continue to proliferate, which will negatively impact the effectiveness of antibiotics. Several techniques have already been employed to eliminate CEC from aquatic ecosystems. Among them, advanced oxidation processes (AOPs) have gained significant attention in recent years. It has been reported that carbon-based materials can serve as efficient adsorbents, catalysts, or catalyst support in these processes. For instance, in our recent study, a biochar derived from agricultural residues was shown to effectively activate peroxymonosulfate (PMS) and degrade amoxicillin, achieving a removal efficiency of 95.0% within just 45 minutes of treatment [3].

In this same context, the work here presented aims to study an advanced oxidation process (AOP) combining PMS, activated by biochar derived from biomass waste. The biochar was produced from the shell of dried fruit widely consumed in the world (*Pistacia vera*), by pyrolysis with different temperatures (500, 700, and 850 °C) under N_2 (1 Kg/cm^2). With the biochar, test experiments were conducted to evaluate its performance as both adsorbent and photocatalyst for the simultaneous removal of *E. faecalis* and Tetracycline (TC). The inactivation of *E. faecalis* and TC degradation through the different photocatalytic processes studied was carried out using a batch reactor containing 100 mL of simulated wastewater enriched with 10^6 CFU/mL of *E. faecalis* and 10 ppm of TC. A range of biochar doses from 0.1 g/L to 2 g/L was added to the reactor, combined as needed with PMS concentrations ranging from 0.01 to 1 mM. The experiments were conducted in 250 mL beakers under continuous stirring at an average speed of 500 rpm. All photocatalytic experiments were performed using a solar simulator (SUNTEST CPS Hereaus) equipped with a 1500 W xenon lamp (0.5% of UV-B and 5 to 7% UV-A). Additionally, the device is equipped with an air-cooling system and a support with water inlet and outlet, ensuring that the reaction temperature remains stable between 25 and 30 °C.

The initial results from the adsorption experiments showed complete inactivation (5.4 log) of *E. faecalis* in less than 60 minutes in simulated water. TC degradation reached between 25% and 30% after 120 minutes. These findings suggest a higher reactivity toward *E. faecalis* compared to TC removal. Building on these promising results for the inactivation of *E. faecalis*, the study is currently being continued, particularly with tests on the photocatalytic activity of the various biochar obtained and the combination of the biochar with PMS under solar radiation. We also plan to carry out specific chemical surface modifications of the biochar to introduce more functional groups and catalytic elements such as iron. These enhancements are expected to significantly improve both the photocatalytic performance and the activation of PMS, ultimately leading to better simultaneous removal of both contaminants.

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This work has received financial support from Spanish MCIN/AEI/10.13039/501100011033 and "ERDF A way of making Europe", through project PHOTORAS (PID2021-128165OA-I00). The authors gratefully acknowledge the Ministry of Higher Education, Research and Innovation, Senegal, for his mobility grant allocated to CG during this work and the support of Universidad Politécnica de Madrid.

P-66

How interface engineering influences the activity of photoelectrodes in solar energy conversion efficiency

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Advances in photoelectrode materials are central to unlocking potential of next-generation renewable energy conversion and storage technologies [1]. This work underscores how strategic interface engineering in a $Bi_2S_3/BiVO_4/ZnO$ ternary heterojunction photoanode achieves remarkable enhancement in solar water splitting. The architecture employs 3D-branched ZnO nanobundles (NBs) as an efficient light absorption and electron transport layer, offering a much larger surface area than conventional 1D nanowires [2]. Whereas the $BiVO_4$ layer acts as the secondary photosensitizer active in the visible region. The Bi_2S_3 layer plays as a dual-functional role, extending the light absorption into the near-infrared region and passivating the surface defects in underlying active layers of $BiVO_4/ZnO$. This passivation effect dramatically reduces trap-assisted charge recombination, enabling a highest photocurrent density of 4.45 mA cm^{-2} at 1.2 V vs. reversible hydrogen electrode (RHE) in sulfate-containing electrolyte solution. This phenomenon is verified employing time-resolved absorption spectroscopy (TAS) and surface photovoltage (SPV). Additionally, the staggered band arrangement between the constituent semiconductors of the multicomponent system is revealed utilizing the ultraviolet photoemission spectroscopy (UPS) and SPV. This energy band alignment is known for its efficient electron transfer, which is pathing from Bi_2S_3 through $BiVO_4$ to ZnO, improving the charge separation. Furthermore, comprehensive materials characterization (refer to **Fig. 1**) validates the structural, morphological, and chemical properties of this engineered interface. In summary, this work presents the synergistic role of spectral photoresponse extension and interface engineering for semiconductor-based photoanode in achieving efficient solar water splitting.

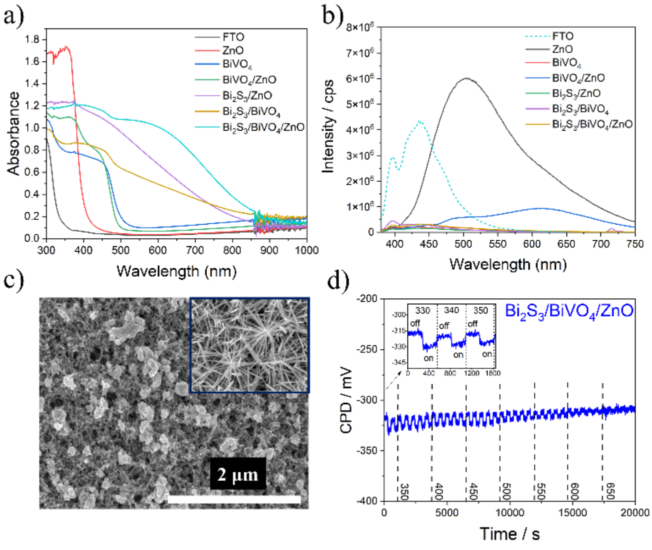

Fig. 1. a) Absorption spectra and b) Time-resolved absorption spectra of all samples, c) SEM image (inset image pertains to ZnO NBs) and d) SPV curve of $Bi_2S_3/BiVO_4/ZnO$ ternary heterojunction photoanode.

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Acknowledgements

The major part of this work is supported by the National Science Centre, Poland (Project no. 2023/50/E/ST5/00679), with additional funding provided by the Ministry of Education, Youth and Sports of the Czech Republic DKRVO (RP/CPS/2024-28/007) and INTER-EXCELLENCE (LTT20010).

Anaerobic thermally assisted photocatalytic methanol dehydrogenation in the presence of water vapour: Engineering SrTiO3 photocatalysts.

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The selective photocatalytic dehydrogenation of methanol into value-added products such as formaldehyde, methyl formate, and green hydrogen offers a sustainable route for their production at industrially relevant scales [1]. $SrTiO_3$ is a widely studied semiconductor photocatalyst due to its thermal and chemical stability, as well as its nearly limitless potential for modification [2]. However, despite over 50 years of research in semiconductor photocatalysis, no industrially relevant applications have been realized, which is caused by insufficient efficiencies and consequently high costs [3].

In this contribution, two strategies to enhance the photocatalytic activity and to control the product distribution in methanol dehydrogenation will be presented. Using a continuous-flow gas-phase flat-plate reactor to approach industrially relevant conditions previously described by Deitermann [4], we will discuss the impact of the cocatalyst/semiconductor interface using Pt and Cu core–Pt shell cocatalysts leading to an increase in AQY by 33%. Moreover, we will reveal the impact of the acid-base properties of $SrTiO_3$ surfaces on the product distribution and overall activity (Fig. 1). The catalytic data are supplemented by an extensive materials characterization using UV-Vis spectroscopy, CO-adsorption DRIFTS, TEM, EDS, UV-Raman spectroscopy, CO_2 and NH_3 TPD, and Kelvin probe measurements. Overall, we will present our recent understanding of underlying structure-activity correlations in thermally-assisted photocatalytic methanol dehydrogenation using $SrTiO_3$ and provide guidelines for potential optimization strategies to further increase the activity and selectivity of the process.

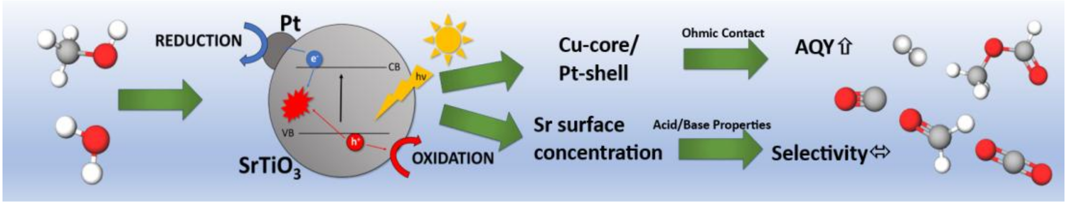

Fig. 1. Modification approaches of $SrTiO_3$ photocatalysts for optimization of photocatalytic activity and selectivity in MeOH dehydrogenation

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P-69

Fabrication and Characterization of WO_3-based gas sensors

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Gas sensors play an indispensable role in monitoring and assessing air quality across various indoor and outdoor environments. The ability to reliably detect and quantify concentrations of toxic, hazardous, and combustible gases is crucial for applications ranging from air pollution control to industrial safety and medical diagnostics. Among the wide array of sensing materials, metal oxide semiconductors have emerged as particularly promising for gas sensor technologies due to their low cost, ease of fabrication, high sensitivity, and long-term stability [1, 2]. Within this group, tungsten trioxide (WO_3) has garnered significant research interest owing to its excellent gas-sensing properties [3, 4].

This study focuses on the synthesis of WO_3 thin films using both spray pyrolysis and pulsed reactive mid-frequency magnetron sputtering (MFMS). In the spray pyrolysis (SP) process, WO_3 films were deposited at 450 °C on soda-lime glass substrates coated with a SiO_2 layer, using a peroxotungstic acid solution and post-annealed in air at 550 °C for 2 hours [5]. In the pulsed reactive MFMS, WO_3 films were deposited on unheated substrate in Ar + O_2 mixture [6]. Similarly, WO_3 films fabricated by pulsed reactive MFMS were annealed at 450 °C for 2 hours in air.

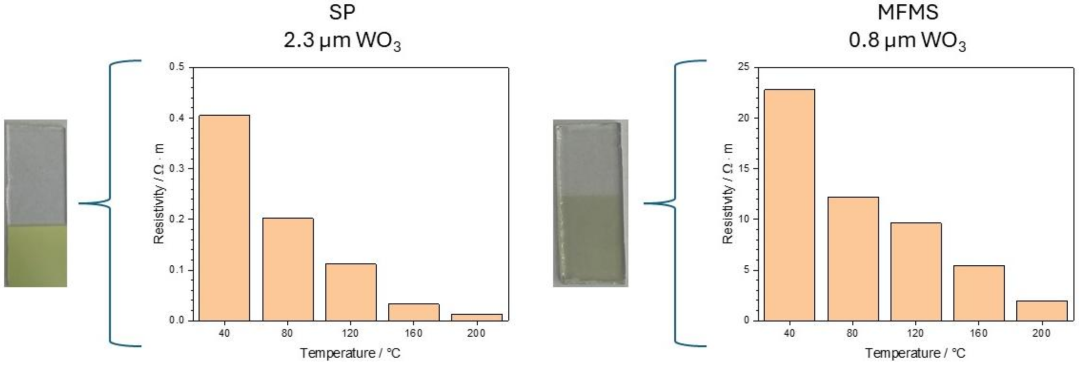

Fig. 1 Dependence of resistivity on temperature for two WO_3 films: 2.3 µm thick WO_3 layer deposited on soda-lime glass with SiO_2 underlayer and annealed at 550 °C for 2 h in air (left) and 0.8 µm thick WO_3 layer deposited on fused silica by pulsed reactive MFMS and annealed at 450 °C for 2 h in air (right).

As shown in Fig. 1 the WO_3 layers deposited by both SP and pulsed reactive MFMS exhibited a decrease in resistivity with increasing temperature, which aligns with the expected behaviour of semiconducting materials. Notably, the resistivity of films prepared by SP was approximately fifty times lower than that of the layers deposited by pulsed reactive MFMS. This variation in resistivity is particularly advantageous for gas-sensing applications, as certain target gases may either increase or decrease the resistivity of the sensing material upon adsorption. Thus, having access to layers with different baseline resistivities allows for better tuning of sensor response depending on the type of analyte – low-resistivity films are more suitable for detecting oxidizing gases (e. g. NO_2) that increase resistance, while high-resistivity films may be more responsive to reducing gases (e. g. H_2 or CO) that lower resistance. These findings suggest that WO_3 films prepared by both techniques have promising potential for use in gas-sensing applications, with the possibility to tailor sensor properties by selecting the appropriate deposition method.

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This work was supported by the project "Sensors and Detectors for Future Information Society – SENDISO reg. n. CZ.02.01.01/00/22_008/0004596" by the Programme Johannes Amos Comenius, call "Excellent Research".

Synthesis of MoS_2 and Its Photocatalytic Application in Ciprofloxacin Degradation

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Molybdenum disulfide (MoS_2), a transition metal dichalcogenide has attracted considerable attention as a photocatalyst due to its suitable bandgap (1.3-1.9 eV), high chemical stability, and environmental friendliness [1]. However, agglomeration and low reusability limits its application on large-scale photocatalytic water treatment. Therefore, recent research has been focused on minimization of these challenges [1,2].

In the present study, MoS_2 was synthesized using hydrothermal method. The precursor used for the synthesis are sodium molybdate dihydrate and thiourea as molybdenum and sulphur sources, respectively. The precursors were dissolved in deionized water and stirred to obtain a homogeneous solution. The solution was transferred into Teflon-lined stainless-steel autoclave and temperature of 200 ^oC was maintained for 12 h. The autoclave was cooled at room temperature and black precipitate was collected and thoroughly washed with water and ethanol and dried at 90 ^oC for 12 h. The resulting MoS_2 powder exhibited a characteristic black colour.

The photocatalytic activity of the synthesized MoS2 was evaluated by observing the degradation of a common pharmaceutical, ciprofloxacin (CIP), in deionized water under the UV LEDs light irradiation (365 nm). The initial concentration of CIP was 10 mg/L, whereas the concentration of the catalyst was 0.5 g/L and the suspension was stirred to maintain uniform dispersion. Initially, the solution was stirred in the dark for 30 minutes to achieve adsorption -desorption equilibrium. During the photocatalytic reaction, aliquots were taken at regular time interval and analysed using a UV-Vis spectrophotometer in the range of 200-500 nm to monitor CIP concentration. Moreover, total organic carbon (TOC) analysis was performed using a TOC analyser to evaluate the rate of mineralization. Experimental results showed approximately 50 % reduction in CIP concentration within 120 minutes of UV irradiation, while 10 % TOC removal was observed shows partial mineralization.

The results indicates that MoS_2 has potential to degrade the ciprofloxacin but also highlight the further need for the optimization of the properties to improve the degradation and mineralization efficiency.

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Funding for this work was provided by the Slovenian Research and Innovation Agency (ARIS) within the framework of Young Researcher program, research program group P1-0134, and project L7-1848, J2-4444 and N2-0310.

P-71

Pattern-illumination Time-resolved Phase Microscopy and its Applications for Photocatalytic and Photovoltaic Materials

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The pattern-illumination time-resolved phase microscopy (PI-PM) method is a technique used to study the microscopic charge carrier dynamics in photocatalytic and photovoltaic materials.[1] The method involves illuminating a sample with a pump light pattern, which generates and decays charge carriers due to trapping, recombination, and transfer processes. The distribution of photo-excited charge carriers is observed through refractive index changes using phase-contrast imaging. In the PI-PM method, refractive index change is selectively monitored by adjusting the focus position and enhance sensitivity to the phase change of photo-excited charge carriers, providing the observation of non-radiative processes, such as charge diffusion, trapping to defect/surface states, and interfacial charge transfer of photocatalytic and photovoltaic reactions. The quality of the image sequence is recovered using a statistical/mathematical calculation. Categorizing and mapping different types of charge carriers based on their response profiles using clustering analysis, provides spatial information on charge carrier types, and the identification of local sites for efficient and inefficient photo-induced reactions, providing valuable information for the design and optimization of photocatalytic materials such as the cocatalyst effect.

There are several key points to this method: the noisy image due to pulse-light imaging is recovered by mathematical and statistical calculations called "total-variation regularization"; the carriers trapped at the surface/defect states are efficiently observed by the refractive index detection, which are not observed directly by the transient absorption or time-resolved photoluminescence; different types of carriers on a surface are distinguished by the sign of the refractive index change and the distribution change due to scavengers (electrons / holes).

One of our recent result is shown here. This study investigates charge carrier dynamics in mixed-dimensional $CsPbBr_3$ perovskite materials, prepared using varying molar ratios of $PbBr_2$ and CsBr in precursor solutions. By employing the PI-PM method, we provide spatially and temporally resolved insights into the transition from 2D to 3D perovskite structures. Our results reveal distinct charge carrier behavior, with 2D perovskites dominated by hole dynamics and 3D perovskites dominated by electron dynamics. The structural transition, driven by increasing CsBr content, leads to the formation of larger crystalline objects. Furthermore, we demonstrate that combining 2D and 3D perovskites enhances charge separation, prolonging hole lifetimes in the 2D regions. (Fig. 1)[2]

Another study employs the PI-PM method to capture the intricate dynamics of charge carriers in the presence of co-catalysts. Through meticulous experimental design and analysis, we have elucidated the mechanisms by which co-catalysts such as platinum (Pt) on titanium dioxide (TiO_2) and cobalt-phosphate (CoPi) on hematite influence charge carrier behavior, including localization, distribution, and decay rates. We could clearly locate the electron accumulated region by Pt deposition on TiO_2 and hole accumulation on CoPi cocatalysts on hematite by identifying the charge carrier dynamics affected by different scavengers.[3] From these results, the PI-PM method is unique and powerful tool, which is different from the other time-resolved techniques.

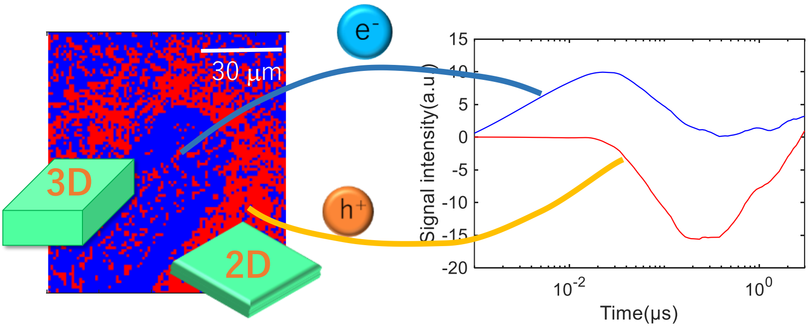

Fig. 1. A categorized map of charge carrier behavior of electrons and holes around a 3D perovskite surrounded by 2D perovskite layers. 3D accumulated electrons, while 2D is dominated by holes.

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Photocatalytic Activity and Stability of Carbon Nitride-Pyrite Composites

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Photocatalytic water splitting is a possible contender to improve drawbacks of relying on a single hydrogen generation technologies. If a material is not suitable for overall water splitting (OWS), it can also be used for just one part of the reaction, for example the hydrogen evolution (HER). In this case a sacrificial agent such as methanol can be used as a hydrogen source. The main advantage to proceed research in photocatalysis is the direct storage of sunlight into a chemical.[1]

Carbon nitrides (CN), especially graphitic carbon nitride, is one of the most discussed photoabsorbers in the research community. The properties make CN suitable for photocatalysis due to its color (yellow), chemical stability, low production cost, non-toxicity and overall resilience. [2]

Nonetheless, our recent work [3] has revealed a significant limitation: Photo-induced self-degradation in defect-rich graphitic carbon nitride containing heptazine units can lead to ammonia release from the material. To assess whether this phenomenon is a broader issue within carbon nitrides—particularly in the context of nitrogen reduction reactions—we compared defect-rich graphitic carbon nitride with a crystalline carbon nitride composed mainly of triazine units, containing lithium cations and chloride anions, called PTI [4]. This material was then investigated for its stability and photocatalytic performance [5].

We will present the photostability and catalytic activity of defect-rich graphitic carbon nitride and compare them with PTI. Ion chromatography results showed improved stability of the PTI in comparison to the VN-CN after light exposure.

To reduce charge carrier recombination, we introduced a co-catalyst, pyrite (FeS_2), synthesized via solvothermal microwave assisted methods. FeS_2 was loaded with 1, 5, and 10 wt% onto the carbon nitrides. The combination with the co-catalyst enhanced the hydrogen production in both types of carbon nitrides. While graphitic carbon nitride continues to suffer from self-degradation, the crystalline PTI demonstrates far greater stability. [5]

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We acknowledge funding by the DFG Priority Program 2370 Nitroconversion (501901537).

Effects of REEs doping and co-doping on crystal structure, phase and photocatalytic performance of TiO_2

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Rare earth elements (REEs) as dopants draw attention for enhancing the properties of titanium dioxide (TiO_2). They can favour substrate adsorption, increase the efficiency of electron and hole separation, and tune the band gap due to their unique electron structure [1, 2].

Polycrystalline well-crystallized powders, consisting of roundly elongated particles based on TiO_2 doped with Sm, Gd, Tb, Tm, Yb or co-doped with Sm/Gd, Sm/Tb, Sm/Tm, Sm/Yb, were successfully synthesized using a straightforward, template-free one-step hydrothermal method. This process employs using titanium butoxide as a precursor in aqueous solutions, making it cost-effective and environmentally friendly.

The similar morphology of undoped, mono- and co-doped TiO_2 was confirmed by SEM analysis. Investigations of the samples using EDS and XPS methods showed the presence of titanium, oxygen, carbon and the corresponding RE with homogeneous distribution. XRD and Raman techniques indicated the mixed phase of anatase-brookite in the samples that can favour photocatalytic activity due to the electrons transfer from the more cathodic conduction band of brookite to the anatase conduction band and thus, resulting in effective electron–hole separation [3]. The ratio between Raman vibrational modes for doped and undoped powders was similar, indicating that the fraction of specific exposed facets in the samples does not change due to modification. According to XRD analysis, no RE-based secondary phase was detected in the samples, which can be attributed to their small amount. The presence of RE in the powders in the trivalent forms was revealed by XPS analysis.

The intensity of XRD peaks for modified samples decreased compared to pristine TiO_2, which can be attributed to structural defects and distortion in the crystal lattice. Higher angles peak shifting is observed in the XRD patterns for all samples meaning compression and reduction in the average lattice parameters that was confirmed by calculations. These changes can relate to the incorporation of the RE as oxides on the surface of TiO_2.

It was established, that mono-doping inhibited the crystallites growth (from ~ 9.1 nm to ~7.4 nm) whereas co-doping enhanced their size (up to ~11 nm). That was confirmed by the Scherrer equation, the Williamson-Hall analysis, the Size-strain plot, the Halder-Wagner methods, and transmission electron microscopy. These results are also in good agreement with the BET analysis. The surface areas of mono-doped samples lie in the range of 183-194 m^2/g and 156-165 m^2/g for co-doped powders. The type IVa of isotherms and H2b type of hysteresis loops were observed for the samples and confirmed their mesoporous structure.

Compared to the pristine TiO_2, the UV–Vis DRS spectra of the doped samples were shifted to the visible region. Absorption peaks for the samples containing Tm were observed in the visible region at 685 and 792 nm, which can be attributed to the f–f electron transition of RE^{3+} or 4f electron transitions of RE ions.

Photocatalytic activity of the synthesized samples was studied in the reactions of diclofenac and Rhodamine B degradation under UV and visible light. The photocatalytic performance of doped samples was higher compared to TiO_2. RE because their f-orbitals can form impurity bands and trap the electrons reducing recombination with holes and prolonging lifetime of charge carriers favouring the photocatalytic activity. Among the doped powders the mono-doped ones were more active than co-doped ones. The enhancement of their photocatalytic activity relates to the more developed porosity, higher surface area and smaller crystallites.

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This work was supported by the SARU-fellowship program for researchers at risk from Ukrainian universities and by the Technical University of Denmark. This work was partially supported by the Wallenberg Initiative Materials Science for Sustainability (WISE), funded by the Knut and Alice Wallenberg Foundation.

P-74

Zr-MOFs based Heterojunction for Enhanced Photocatalytic Methane Oxidation with Nearly 100% Selectivity

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Direct selective oxidation of methane (DSOM) under mild conditions and achieving total selectivity in methane hydroxylation remains elusive due to the competitive CO_2 formation. The key to DSOM lies in tuning the band structure of the photocatalyst to enable controlled generation of reactive oxygen species (•OH, •OOH, etc.) within an optimal range. [1] While metal oxides or metal/oxide catalysts are commonly used in DSOM, these semiconductor structures are often limited by their simplicity, making it challenging to fine-tune their band structures. Compared to other materials, MOFs exhibit well-defined structures, excellent light absorption and efficient charge carrier separation, making them outstanding candidates for photocatalysis. In this study, we utilized the synergistic effect on a formed heterojunction between Zr-based MOFs U6-X (X=NH_2 and H) and P25 type TiO_2 to significantly enhance the photocatalytic methane oxidation performance while effectively suppressing the formation of overoxidized byproducts such as CO_2. Under optimized reaction conditions, the U6-H/P25 based type I heterojunction achieved an outstanding target product yield of 2675.6 μmol g_{cat}^{-1} with nearly 100% selectivity, outperforming other reported inorganic heterojunction catalysts.

The U6-X/P25 samples were prepared using an *in situ* synthesis method. The structures of U6-X/P25 were characterized by XRD, TEM, XPS, XAS, IR, EPR, Raman, UV-VIS, PL, etc. Photocatalytic CH_4 oxidation tests were conducted in a batch photoreactor using CH_4 and Air mixtures under full-spectrum irradiation from a 500 W Xe lamp at 20 ℃. The liquid and gaseous products were analyzed using NMR and GC, respectively. [2]

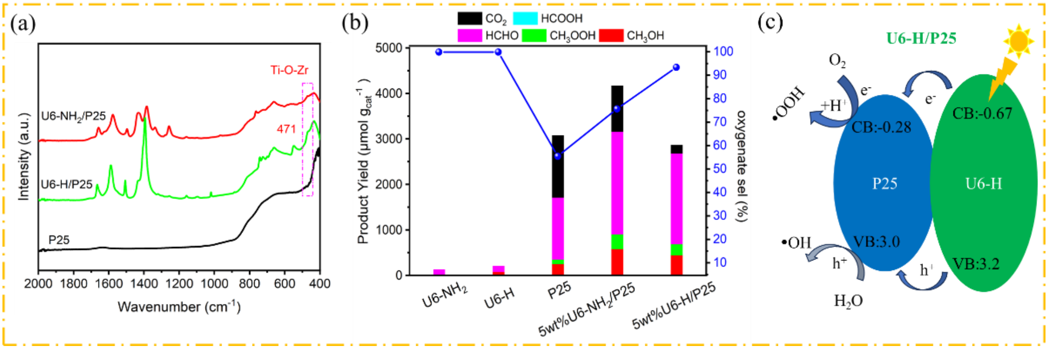

Fig. 1. (a) IR of U6-X/P25, (b) Photocatalytic CH_4 oxidation performance, and (c) Proposed mechanism over U6-H/P25

Various characterizations have confirmed the successful construction of the corresponding heterojunctions between U6-X and P25, accompanied by the formation of the Ti–O–Zr interface (Fig. 1a). As shown in Fig. 1b, P25 produces a certain amount of oxygenates but suffers from a relatively low oxygenate selectivity of 55.4%. In contrast, both U6-NH_2 and U6-H effectively suppress CO_2 formation but exhibit a limited DSOM activity. When U6-NH_2 is combined with P25 to form a Z-scheme heterojunction, the oxygenate yield increases, with the selectivity rising to 75.6%. Compared to U6-NH_2/P25, the type I heterojunction of U6-H/P25 achieves a comparable oxygenate yield, while the selectivity further improves to 93.3%. Under optimal conditions, it delivers an oxygenate yield of 2675.6 μmol g_{cat}^{-1} with nearly 100% selectivity. Compared to the Z-scheme structure of U6-NH_2/P25, which features a relatively high conduction band (CB), the type I heterojunction of U6-H/P25 not only enhances charge carrier separation efficiency but also directs electrons to the lower CB of P25. This suppresses the excessive generation of •OOH and effectively reduces the overoxidation of oxygenates into CO_2 (Fig. 1c). This synergistic effect in the type I heterojunction enables efficient methane activation, while simultaneously preventing overoxidation of the target products.

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Acknowledgements

This work has received financial support from the PulseCOMeth (ANR-22-CE50-0018) project.

Enhanced Photocatalytic Hydrogen Evolution Under Visible Light Using g-C3N4/NiFe Prussian Blue Analog Composites

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H_2 produced via photocatalytic water splitting shows great potential as a renewable alternative to fossil fuels; however, increasing the H_2 production efficiency remains challenging. In this study we synthesized various graphitic carbon nitride–Prussian blue analog (GCN-PBA) heterostructure composites using PBAs containing different transition metals (Ni, Co, and Fe) and analyzed their visible-light absorption and H_2 production efficiency. We believe that our study makes a significant contribution to the literature because the GCN-NiFe heterostructure composite exhibited excellent visible-light-induced H_2 production efficiency, making it a promising candidate for practical applications in solar H_2 production. Moreover, we propose a potential mechanism for the observed photocatalytic activity, which can contribute to the design and optimization of efficient photocatalysts for solar H_2 production, promoting the advancement of renewable energy technologies.

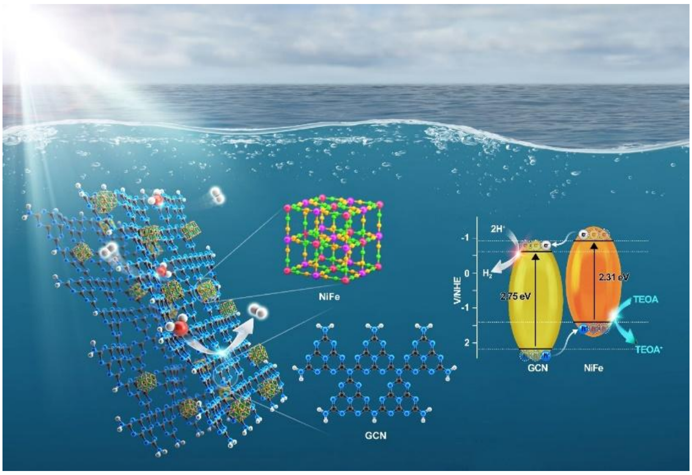

Fig. 1. Schematic illustration of the proposed photocatalytic activity mechanism.

The study proposes a band structure and type II heterojunction mechanism for GCN-NiFe composites to explain their enhanced visible-light-driven H_2 production. The energy-level diagram shows that the conduction band edges of both GCN and NiFe lie above the reduction potential for H_2, while NiFe's valence band lies below the oxidation potential of water. This alignment allows efficient separation and transport of photogenerated electrons and holes. Under visible light, NiFe generates charge carriers that are effectively separated within the GCN-NiFe structure, with electrons migrating to GCN to drive H_2 evolution. Meanwhile, the holes are consumed by electron donors, contributing to the composite's high photocatalytic efficiency.

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This research was funded by the Nuclear Safety Research Program through the Korea Foundation of Nuclear Safety (KoFONS) using financial resources granted by the Nuclear Safety and Security Commission (NSSC) of the Republic of Korea. (No. 00231329).

Effect of reaction temperature on production of high concentrations of H_2O_2 over C_3N_4 photocatalyst

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H_2O_2 is a versatile compound that has gained attention in various fields, including the synthesis of pharmaceuticals and organic functional materials, as well as its potential use as an energy carrier [1] to replace hydrogen. Additionally, H_2O_2 is considered a green chemical due to its decomposition into water and O_2. However, the current industrial manufacturing method, known as the anthraquinone method [2], involves a multi-step synthesis process, the use of toxic organic solvents, and the production of explosive gases. Therefore, there is a need for a simpler and more environmentally friendly synthetic method. One promising method being studied is the photocatalytic method [3]. It is important to continue researching and developing photocatalytic methods to meet the demand for more sustainable synthetic methods. Photogenerated electrons can reduce O_2 to produce H_2O_2 over various photocatalysts. Visible light-driven photocatalysts, such as WO_3, are favorable because H_2O_2 decomposes under UV light. In this study, we investigated the production of H_2O_2 through the two-electron reduction of O_2 in a 2-propanol (IPA) suspension of C_3N_4 photocatalyst. Our findings indicate that the rate of H_2O_2 production significantly increases with a slight elevation in temperature due to thermal acceleration of the photocatalytic reaction. This study aims to analyze the mechanism of this reaction to achieve more efficient production of H_2O_2.

C_3N_4 powder (50 mg) was suspended in IPA (5 mL) in a test tube and the gas phase was placed with O_2. The test tube in a glass-type water bath kept at various temperatures was irradiated with visible light (lambda > 400 nm) using a Xe lamp equipped with an L-42 cut filter. After the reaction, O_2 in the gas phase and acetone in the liquid phase were analyzed by gas chromatography, while a potassium iodide reagent (WAK-H2O2(C), Kyoritsu Chemical-Check Lab., Kanagawa, Japan) was used to color the H_2O_2 in the liquid phase.

Fig. 1a depicts the time courses of photocatalytic H_2O_2 production by O_2 reduction in an IPA suspension of C_3N_4 at different temperatures under visible light irradiation. We confirmed by blank reactions that C_3N_4 and light irradiation were indispensable for producing H_2O_2. At 25°C, the H_2O_2 concentration reached 3.2 mM at 4 h. Fig. 1a also shows that a slight increase in reaction temperature significantly enhanced both the rate of H_2O_2 production and the concentration of H_2O_2. The concentration at 60°C (22 mM at 4 h) was seven-times larger than that at 25°C. Notably, the increase in H_2O_2 concentration with an increase in temperature by 10°C from 50°C to 60°C was considerably greater than the increase in H_2O_2 concentrations with increases in temperature by 10°C in other temperature ranges. As shown in a figure inserted in Fig. 1a, H_2O_2 production at 60°C continued after 4 h and the concentration of H_2O_2 reached ca 34 mM after 8 h, which is considerably larger than those of previously reported C_3N_4.

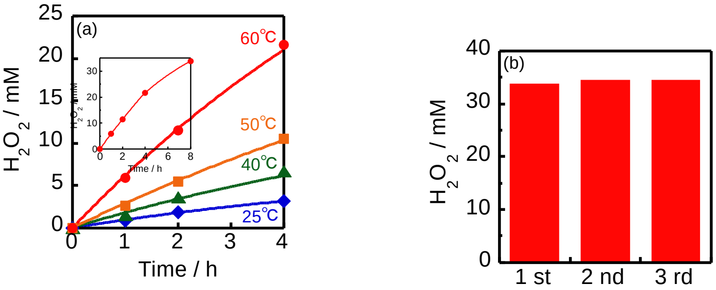

Fig. 1 (a) Time courses of photocatalytic H_2O_2 production by O_2 reduction in a 2-propanol suspension of C_3N_4 at various temperatures under irradiation of visible light and H_2O_2 production at 60°C for a prolonged time (inserted figure). (b) Durability tests at 60°C for 8 h.

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Acknowledgements

This work was partly supported by JSPS KAKENHI Grants 23K17964, 23H01767 and 22H00274.

P-77

Evaluation of Muscovite as a Photocatalyst in Aqueous Methanol Solution under UV Light

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Given the global issues of increasing energy consumption, depletion of fossil fuels, and environmental pollution caused by human activities, it is crucial to explore new ways of obtaining and storing clean energy sources. Hydrogen production appears to be a very promising solution to replace fossil fuels with minimal environmental impact, while also serving as a key chemical compound in various industrial processes, such as ammonia synthesis and hydrorefining [1].

Clay minerals are eco-friendly materials that help adsorb contaminants and improve the activity of nanomaterials. When used as supports for semiconductor photocatalysts, clays significantly improve both the photocatalytic efficiency and recyclability compared to standalone semiconductor nanomaterials. Among clay minerals, muscovites from the mica group are commonly used for their chemical and physical stability as flexible ultrathin insulating substrates, as well as wide-bandgap layered semiconductors for 2D electronic devices [2].

Muscovite samples Ms1 and Ms2 were prepared to the particle size fraction less than 0.04 mm by milling (a vibratory mill VM4 OPS Přerov, Czech Republic) at 1500 rpm for 2.5 min and then sieving. Nickel(II) nitrate hexahydrate Ni(NO3)2·6H2O was supplied by the company Lach-Ner Co., Neratovice, Czech Republic. Muscovites were calcined at 600 °C to the Ms1/600 and Ms2/600 samples. The NiO/muscovite composites containing about 20 wt.% NiO originated from Ni(NO3)2·6H2O as a metal precursor were obtained by solid state thermal synthesis at 600 °C.

The aim of this study was to synthesize NiO/muscovite photocatalysts through various preparation methods, aiming to create stable, low-cost, environmentally friendly, and efficient materials for photocatalytic hydrogen generation. The photocatalytic activity was investigated in a stirred photoreactor under 254 nm light irradiation using a methanol–water mixture as the sacrificial agent. A comprehensive set of characterization techniques was employed, including X-ray diffraction (XRD), scanning electron microscopy (SEM), coupled with energy-dispersive X-ray spectroscopy (EDS), specific surface area analysis (BET), UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), photoluminescence spectroscopy (PL). The results of the photocatalytic experiments are presented in Figure 1 and show a clear correlation with the physicochemical properties derived from these characterization techniques.

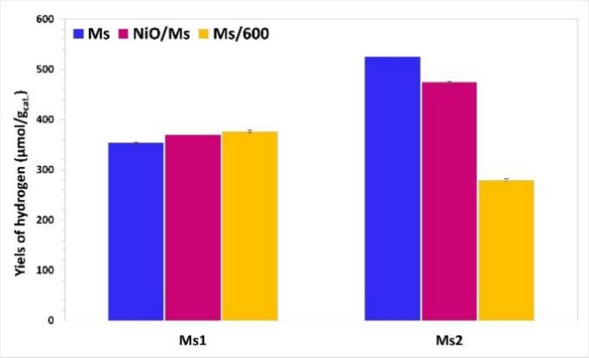

Fig. 1. Photocatalytic action of muscovites in MeOH50.

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The work was supported by Large Research Infrastructure ENREGAT projects No. LM2023056 and the European Union under the REFRESH - Research Excellence For REgion Sustainability and High-tech Industries project No. CZ.10.03.01/00/22_003/0000048 via the Operational Programme Just Transition.

Preparation and Characterization of Tungsten Oxide Thin Films by Modified Sol-Gel Inkjet Printing for Photoelectrocatalytic Applications

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Tungsten oxide is currently a widely studied inorganic semiconductor known for its remarkable chromogenic properties. It is used in the production of photochromic glass, various sensors, memory devices as well as photocatalytic and solar cells. Typically, tungsten oxide layers are produced by costly and complex techniques under vacuum.

The aim of this work was to prepare thin films using a modified sol-gel method [1]. The layers were prepared by material printing method using Dimatix printer. In the first part of the work the printing conditions were optimized. The most suitable composition of the printing formulation was investigated applying Owens-Wendt theory method [2] and the best treatment of the substrate itself. The surface tension and dynamic viscosity of the print formulation were measured, and suitable solvents were explored for the chosen deposition technique [3]. According to the results of viscosity and surface tension measurements, the most suitable printing formulations were the mixtures of acetonitrile: ethylene glycol (1:1) and ethanol: ethylene-glycol (1:1). However, after application of the Owens-Wendt theory, the most suitable composition appeared to be the formulation with ethanol: ethylene-glycol.

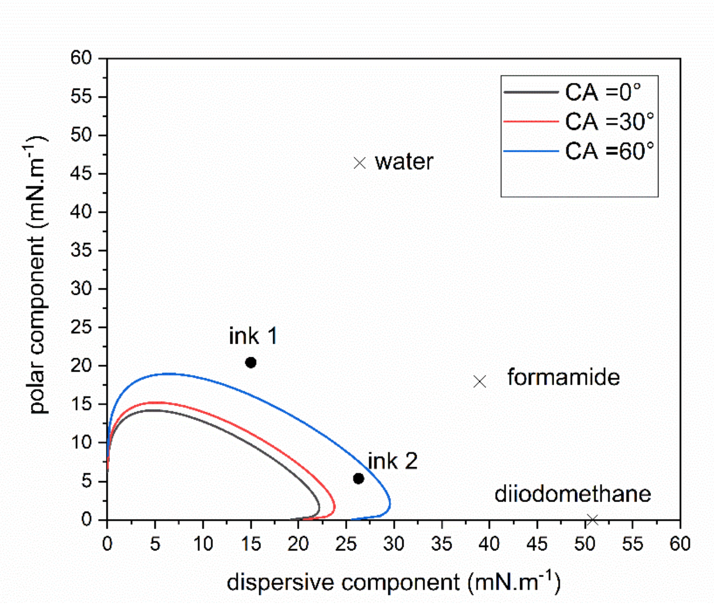

Fig. 1. "Wetting envelope diagrams for FTO glass (ink 1: acetonitrile + ethylene-glycol; ink 2: ethanol + ethylene-glycol) ".

The selected composition was used to prepare a series of samples where the effect of the layer thickness on the resulting electrochemical properties was investigated. The layer thickness was measured with a mechanical profilometer, the crystallinity of the layers was studied using X-ray diffraction and the surface topology was studied by AFM. The photoelectrocatalytic properties were studied by cyclic voltammetry and chronoamperometry, and the influence of layer thickness on the resulting free electron generation was compared.

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This work was supported by Czech Technology Agency through project TH03030197.

P-79

The influence of the substrate on the structural and optical properties of the ordered TiO_2 layers exhibiting a photonic band gap

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Titanium dioxide is an inexpensive, safe, and widely used material that can serve as a photocatalyst, however, its photocatalytic activity is primarily limited to the ultraviolet range of light. Enhancing its activity under visible light is still one of the most important issue in the field of photocatalysis. In recent years, structured layers of TiO_2 have attracted increasing interest due to their unique optical properties. One of the methods of structuring this material involves an inverse opal (IO) architecture. In a classic, ideal opal, spheres with diameters ranging from several tens to hundreds of nanometers form a face-centered cubic (FCC) lattice. In inverse opals, the matrix material fills the voids within the macroscopic FCC network. Owing to the highly periodic arrangement of spherical macropores, IO structures exhibit a photonic bandgap, i.e., a range of energies in which light propagation within the material is forbidden. This effect enhances the interaction time of photons with the material, which can be exploited to improve its photocatalytic activity within selected regions of the light spectrum [1].

In the present study, a series of TiO_2 layers with IO structure were fabricated on selected conductive and insulating substrates. The layers were prepared via self-assembly method using polystyrene nanoparticles of various diameters as a template. The morphology and optical properties were characterized using scanning electron microscopy (SEM) and UV-Vis spectroscopy (Fig. 1 a, b). The photoactivity of the materials was investigated through photoelectrochemical and surface photovoltage (Fig. 1 c) measurements, and photocatalytic tests, supplemented by action spectra recorded in the 330–450 nm range. Terephthalic acid hydroxylation was used as the model reaction.

This work presents the influence of the substrate type on which the inverse opal layers were deposited, as well as the effect of pore size on the structure, spectroscopic properties, and photoactivity of TiO_2 layers. Additionally, a previously undescribed phenomenon—the emergence of multiple photonic bandgaps in materials with larger pore diameters—is discussed.

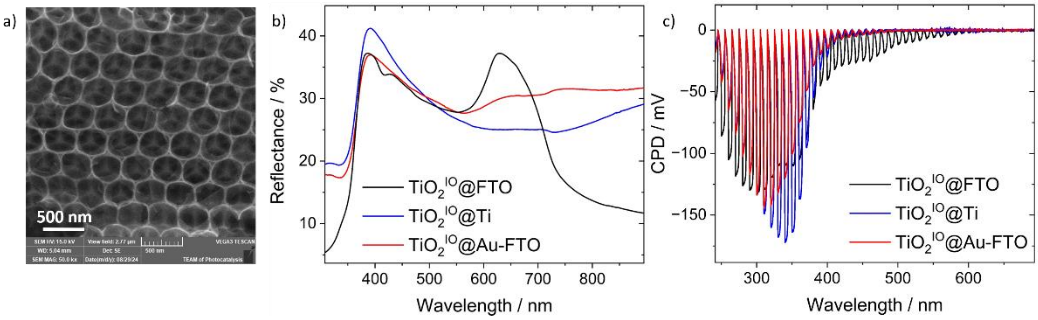

Fig. 1. SEM image of the IO TiO_2 layer (a) and contact potential difference (b) changes upon monochromatic light irradiation (c) of the IO TiO_2 layers loaded on the FTO, Au-FTO and Ti substrates.

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Acknowledgements

This work was supported by the Foundation for Polish Science (FNP) under the TEAM program (POIR.04.04.00-00-3D74/16).

Microstructural and Chemical Analysis of a Tin Sulphide Homojunction Applied in Thin Film Solar Cells

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The growing interest in tin sulphide thin-film solar cells is due to their remarkable advantages: economy, environmental safety, and material availability [1,2]. The chemical and microstructural characteristics of a homojunction fabricated from the synthesis of SnS and SnS:Bi thin films by evaporation and annealing in a sulphur atmosphere were studied in the present investigation. SnS and SnS:Bi films were synthesized using substrate temperatures of 250 °C and 300 °C, an annealing temperature of 40 °C, and an annealing time of 90 min and 120 min. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) techniques were used to study the influence of the synthesis variables on the chemistry and microstructure of the thin films. The results showed that an increase in substrate temperature and annealing time increased the grain size of the thin films. On the other hand, an increase in the annealing time led to the growth of crystalline tin sulphide without the presence of secondary phases. In addition, scanning electron microscopy (SEM) was performed to determine the grain morphology.

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This work has received financial support from the Universidad Industrial de Santander (UIS).

Photocatalytic disinfection efficiency of alkaline earth metal titanates

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Alkaline earth metal titanate perovskites are increasingly used in various industries due to their beneficial properties [1–6]. Their possible environmental impact, however, is rarely investigated, particularly on microorganisms living in or entering surface water bodies.

In this study, calcium titanate ($CaTiO_3$), strontium titanate ($SrTiO_3$), and barium titanate ($BaTiO_3$) photocatalysts were prepared to assess their photocatalytic disinfection efficiency against Gram-negative Escherichia coli and Gram-positive Bacillus licheniformis bacteria. The photocatalysts were characterized using XRD, SEM, DRS, BET, and IR measurements. Additionally, their photocatalytic efficiency was also evaluated by the degradation of phenol. For comparison, commercial alkaline earth metal titanates were used as references. The $SrTiO_3$ we synthesized exhibited significantly higher photoactivity than the $CaTiO_3$ and $BaTiO_3$ (r_0 = 41.60 compared to 4.28 and 10.03×10^{-10} M s^{-1}, respectively), surpassing that of the commercial references. Based on characterization results, this can be attributed to the causal effect of the $SrCO_3$ co-catalyst, higher specific surface area, and more favourable band positions, resulting in higher hydroxyl radical generation. Photocatalytic inactivation results showed that alkaline earth metal titanates (both the reference and hydrothermally synthesized ones) have no or negligible disinfectant effect. Our $CaTiO_3$ and $SrTiO_3$ photocatalysts produced more hydroxyl radicals than our $BaTiO_3$ and the references. For E. coli, our catalysts showed nearly identical disinfectant effectiveness to that of UV-A light (~80% bacterial inactivation over 2 hours). The other catalysts reduced the disinfection efficiency of UV-A light by ~40–70%. This was attributed to the findings that i) these catalysts generated significantly fewer hydroxyl radicals, and ii) the catalyst particles blocked the photons from bacteria. For B. licheniformis, the results were similar but with higher disinfection efficiencies (100% efficiency was observed for UV-A light and for the most effective samples within only 1 hour). In this case, the photocatalytic activity was reduced to an even greater degree (by ~30–100%).

These results may contribute to decision-making when evaluating risks associated with these materials.

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This study was financed by the Bolyai János scholarship (BO/00447/23) provided by the Hungarian Academy of Sciences. The authors acknowledge the 2021-1.2.6-TÉT-IPARI-MA-2022-00009 project. Áron Ágoston acknowledges the Doctoral Student Scholarship Program of the Co-operative Doctoral Program (EKÖP-KDP-24-SZTE-6) of the Ministry of Innovation and Technology financed from the National Research, Development and Innovation Fund. Project no. TKP2021-NVA-19 has been implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-NVA funding scheme.

Efficiency of an advanced oxidation process in the removal of persistent pesticide using an immobilized catalyst

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The advanced oxidation processes (AOPs) represent a promising alternative technology for destruction of pesticides contained in water. The most important of these AOPs is the photocatalysis in presence of catalyst as titanium dioxide nanoparticles.

In the present work, Methomyl, the active ingredient of the commercial pesticide formulations Lannate, is used against many insects including spider mites on fruits and vegetables, and flies in animal/poultry houses and dairies. It is a major ovicide, larvicide, and acaricide, has been studied in a photoreactor containing immobilized layers of titanium dioxide catalyst.

For immobilization of catalyst particles, glass plate has been used as support and four layers have been deposited and dried at 475°C.

Photocatalytic degradation of Methomyl was investigated under 18 W high pressure mercury lamp irradiation. The effect of the distance between irradiation lamp and glass plate, the flowrate, UV light irradiation time, pH solution, different type of catalysts used for Methomyl oxidizing (DT51, EL10, PC105, PC500 and P25) and inorganic ions such as Ca2+ were studied and optimized values were obtained.

Results showed that this process with optimal parameters may lead to an important degradation of Methomyl. Thus, the efficiency of Methomyl elimination increased by decreasing the dose of Methomyl with an optimal flowrate of 122 mL/min, a distance of 5.5 cm and pH = 3, an abatement of 60% has been obtained.

Even though Methomyl was slightly adsorbed on DT51 titanium dioxide catalyst (less than 5%) compared to PC105 titanium dioxide (20%) , the best degradation was observed with DT51 titanium dioxide photocatalyst, where the abatement reached 80%.

Kinetic studies showed that nanoparticles of titanium dioxide P25 were very active in Methomyl degradation and L-H model adequately described the kinetics.

Solar radiations efficiency for removing xenobiotics in presence of a catalyst suspension

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The pollution of surface and grand waters by organic pollutants is caused by discharges of chemical industry, agriculture and daily activities. Organic pollutants affect hormonal or nervous system and resist to biodegradation, which require a constant improvement of water treatment processes.

In the present work, the study focused on the evaluation of solar radiations performances on the degradation of aqueous solution of tylosin, an antibiotic administered to livestock and poultry, in a lab-scale tubular reactor with a suspension catalyst. The tubular reactor with a capacity of 0.3 liter with 26 tubes placed in series was fixed in a rectangular plate. The reactor was positioned facing south in order to ensure maximum energy exchange between the solar radiations and the reaction mixture that flowed out continuously in closed circuit. Tylosin concentration was followed by an UV-Visible spectrophotometer at a wavelength of 290 nm.

Experimental results showed that 1 hour of adsorption, which is a physical phenomenon, 18% of tylosin was eliminated, moreover, with the same exposure time, the abatement of tylosin during photolysis, for an inclination optimal angle of 50°, reached 71% and 100% during photocatalysis. The photocatalysis kinetics was verified by L-H Model. For an optimal degradation of the antibiotic, a low flowrate (120 mL/min), a catalyst dose of 0.3 g/L and a low concentration of tylosin were recommended.

After 1 hour of photocatalysis process, the abatement of tylosin during a cloudy day (84%) was as important as sunny day (100%), which proves that UV radiations pass through the layers of the atmosphere. The study of interaction between tylosin and diazinon, an organophosphorus insecticide generally used as a foliar or soil spray, at different molar ratio[tylosin]/[diazinon] showed that in major cases, when both pollutants were present, tylosin started to be oxidized and diazinon degraded more slowly when the molar ratio decreased from 2 to 1/4.

Advanced Donor–Acceptor Structured Carbon Materials for Sunlight-Driven Hydrogen Peroxide Production via Charge Separation Engineering

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Hydrogen peroxide (H_2O_2) has emerged as a key green oxidant, driving increasing interest in the development of efficient photocatalysts for its sustainable production. In this context, photocatalytic materials incorporating electron donor–acceptor architectures, such as covalent organic frameworks (COFs) and resorcinol–formaldehyde (RF) resins, have recently garnered attention for their favourable charge separation properties under solar irradiation and potential in solar fuel production. However, their application in photocatalytic H_2O_2 generation remains limited. Herein, we report a bipyridine-functionalized polyimide-based COF (PIC-BPY) as a highly efficient photocatalyst for solar-driven H_2O_2 production coupled with pollutant degradation. PIC-BPY exhibited an outstanding H_2O_2 production rate of 2772 μmol g_{cat}^{-1}, which is three times higher than that of its biphenyl-based counterpart. Mechanistic studies, including scavenger tests and electron spin resonance (ESR) spectroscopy, revealed a synergistic redox contribution from the bipyridine units in conjunction with the polyimide framework. Furthermore, hydroxyl radicals generated during the photocatalytic process enabled simultaneous degradation of pollutants, demonstrating the dual functionality of PIC-BPY. These findings highlight the potential of donor–acceptor engineered COFs as integrated platforms for green oxidant production and environmental remediation.

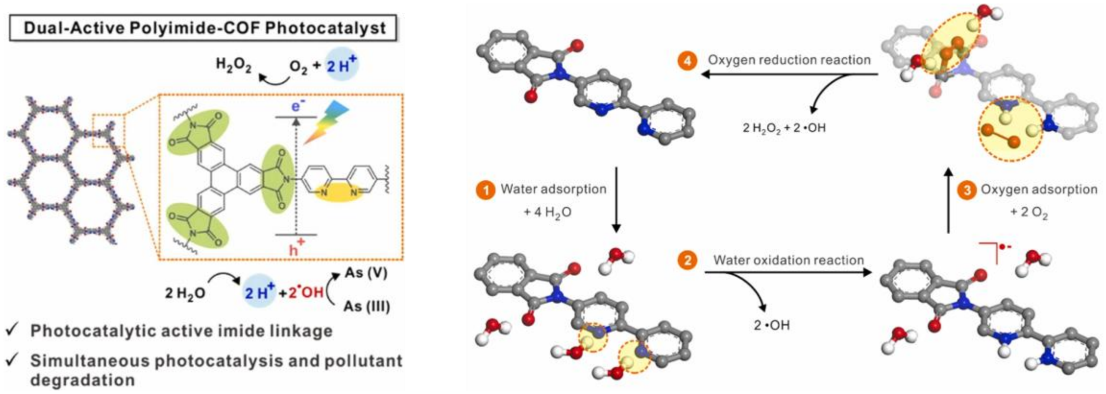

Fig. 1. Schematic illustration of solar energy-driven H_2O_2 production using PIC-BPY.

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Acknowledgements

This work was also supported (in part) by the Yonsei University Research Fund(Post Doc. Re-searcher Supporting Program) of 2024 (project no.: 2024-12-0217).

P-85

Water-soluble ionic carbon nitrides for enhanced photocatalysis and other catalytic applications

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In addition to conventional (non-ionic) carbon nitrides, water-soluble ionic carbon nitrides represent a novel class of poly(heptazine imide) (PHI) materials that enable photocatalysis under quasi-homogeneous conditions. Their superior performance has been demonstrated in photocatalytic hydrogen peroxide (H_2O_2) production. A key advantage of these materials lies in their reversible solubility: by simply adjusting the ionic strength of the medium, the dissolved photocatalyst can be easily recovered and redissolved without any loss of activity or selectivity [1-3].

Recently, we synthesized water-soluble PHI materials incorporating various alkali metal ions, paving the way for a rational design approaching to enhance both photocatalytic activity and stability. The photophysical properties of these materials were investigated using ultrafast time-resolved spectroscopy and correlated with their photocatalytic efficiency in H_2O_2 production.

Additionally, we found that water-soluble ionic carbon nitrides serve as highly effective stabilizers for ultrafine gold nanoparticles (Au NPs) with diameters of 2–3 nm. The stabilized nanoparticles exhibit remarkable dispersibility and exceptional stability even in solutions with high ionic strength. Their catalytic performance was demonstrated in the selective reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$ as a model reaction, where they outperform even benchmark “naked” Au NPs stabilized by an excess of $NaBH_4$ [4].

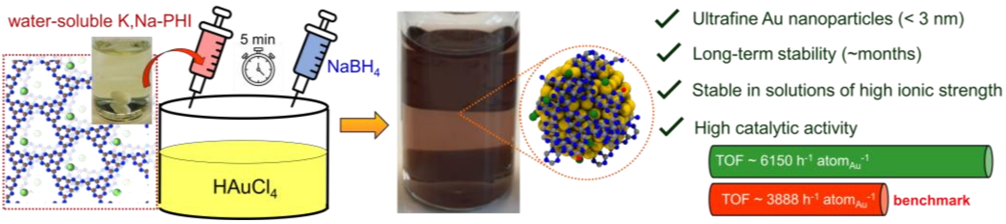

Fig. 1. Concept of effective stabilization of ultrafine Au nanoparticles using water-soluble ionic carbon nitride.

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Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Projektnummer 364549901 – TRR 234 [Projects B6, B7, C2, C4 and Z2] and BE 5102/5-1, by the European Union´s Horizon 2020 research and innovation programme under grant agreements No. 101122061 (SUNGATE), and by the Alexander von Humboldt Foundation through the Humboldt Research Fellowship for I.K.

P-86

Graphitic carbon nitride for Hg(II) photocatalytic removal from aqueous solution: influence of precursor and exfoliation

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Graphitic carbon nitride ($g-C_3N_4$) is an organic semiconductor that has recently received increasing attention for photocatalytic applications. It is a metal-free polymer material, chemical and thermally stable, that can be active under visible light (band gap value of ~2.7 eV). Furthermore, the position of the conduction band edge (E_{CB}) of $g-C_3N_4$ (-1.3 V *vs* NHE at pH 7) [1] indicates this semiconductor can attain the photocatalytic reduction of a variety of metal ions. On this basis, one interesting application of carbon nitrides might be the photocatalytic removal of Hg(II) from aqueous matrixes. This is a topic of great concern due to the high toxicity and bioaccumulation effects of mercury even at very low concentrations [2]. In the present work, $g-C_3N_4$ bulk was synthesized by thermal polycondensation of two precursors, urea (Bulk-U) and melamine (Bulk-M). The bulk samples were further submitted to a thermal post-treatment at 450 and 500°C (Exf-U and Exf-M, respectively) to attain their exfoliation. The materials were characterized by XRD, N_2 adsorption-desorption isotherms at 77 K, scanning electron microscopy (SEM), XPS, FTIR, UV-vis DRS, and photoluminescence spectroscopy. The photocatalytic reactions were carried out both under UVA light (Heraeus TQ-150 lamp) and solar simulated radiation (Solar Box 1500). An aqueous solution of $HgCl_2$ was used as the source of 50 $mg \cdot L^{-1}$ Hg(II) at natural pH (~ 5) with a photocatalyst loading of 0.25 $g \cdot L^{-1}$. Before irradiation, the suspension was kept in the dark for 30 min to allow the adsorption of mercury on the photocatalyst. Tests were done using both ultrapure water (UW) and water collected from the secondary effluent of a wastewater treatment plant (WWTP). Mercury concentration in solution was determined by cold vapor atomic fluorescence spectrometry (CV-AFS).

The characterization of the photocatalysts proved the significant influence of the precursor and the thermal post-treatment on both the physicochemical and electronic properties of the materials and their photocatalytic performance for Hg(II) removal. As an example, Bulk-U and Bulk-M showed S_{BET} values of 33 and 8 $m^2 \cdot g^{-1}$, respectively, which were increased by the thermal post-treatment to 99 (Exf-U) and 28 $m^2 \cdot g^{-1}$ (Exf-M) (**Fig. 1a**). This increase is related to the separation of the stacked layers, also proved with XRD results. In addition, the exfoliation induced a slight increment in the band gap (ca. 7%) in the melamine samples but not in the urea-derived samples.

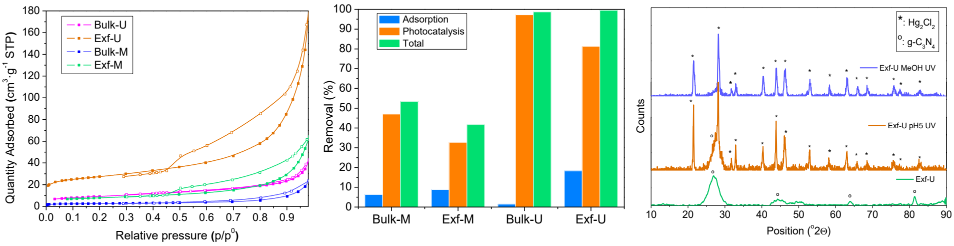

Fig.1. (a) Adsorption-desorption N_2 isotherms for synthesized $g-C_3N_4$; (b) Hg(II) uptake from WWTP water after 3 h of reaction; (c) XRD diffractogram for Exf-U before and after 3 h of photocatalytic reduction of 50 $mg \cdot L^{-1}$ Hg(II) with UV irradiation.

The Hg(II) photocatalytic removal was attained with all the materials by addition of methanol as hole scavenger in those reactions carried out in the UW matrix, and with no scavenger in the water matrix from WWTP. Compared to the samples produced from melamine, those obtained from urea displayed a superior activity for Hg uptake, showing Exf-U the best performance in both water media. It was attained the complete removal of 50 $mg \cdot L^{-1}$ Hg(II) after 3 h in WWTP water, with some contribution of adsorption to the uptake of mercury (**Fig. 1b**). The presence of Hg(II) reduced species over the photocatalyst Exf-U after reaction was investigated by XRD (**Fig. 1c**), which showed the formation of calomelane (Hg(I)), and thus the successful photocatalytic reduction of Hg(II).

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Acknowledgements

The authors thank the funding from AEI and Ministerio de Ciencia e Innovación, PID2021-126400OB-C32); and EU's Horizon 2020 program (Marie Skłodowska-Curie grant) No 101007578.

Preparation of Cu-based TiO_2 and TiO_2/polymeric carbon nitride by hydrogen and nitrogen flow thermal treatment for photocatalytic CO_2 reduction under mild conditions

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In recent years, significant attention has been directed toward tremendous concentration of CO_2 in the atmosphere, which significantly contributes to climate change and global warming. According to the International Energy Institute, in 2023 the highest worldwide CO_2 emission that crossed 40 giga tonnes, came from energy consumption, particularly from the combustion of fossil fuels (87%).[1] In addition, the existing technologies are insufficient to fulfil required reductions in CO_2 emissions. To address this challenge, novel and environmentally friendly solutions can be proposed that enable the reuse of this gas for producing added-value products (CCU-technology).[2] Among these, one of the promising, future-oriented method is photocatalytic reduction, which involves the adsorption of atmospheric CO_2 and its conversion under solar light illumination by using water as the hydrogen source.[3]

Our approach focuses on the material study of reduced Cu-based titania and titania/polymeric carbon nitride porous composites for photocatalytic CO_2 reduction under mild conditions in presence of water vapor, conducted in our custom-made photoreactor. The presented study was centred specifically on obtaining reduced form of copper on as-synthesized anatase and its composite with polymeric carbon nitride under hydrogen or nitrogen flow under elevated temperature. The importance of this study is essential to optimize the reduction conditions of impregnated copper(II) source, as Cu-based catalysts are reported to be the most promising in photo- and photo(electro)reduction of CO_2 toward added-value products such as alcohols and acids.[4] Moreover, the broad studies conducted by several scientists showed that obtaining specifically copper(I) oxide by this method is challenging as the mechanism of reduction of copper(II) requires first nucleation and then formation of reduced phase, where the latter step can result in direct formation of metallic copper rather than Cu_2O due to kinetics.[5-8] Furthermore, the reported findings were usually based on copper oxide species or in presence of commercially available titania rather than synthesized porous anatase. Our catalysts were characterized by X-Ray Diffraction, Raman, UV-Vis and photoluminescence spectroscopy, H_2 temperature-programmed reduction and further tested for photocatalytic reduction of CO_2 by water vapor.

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Acknowledgements

This work has received financial support from BOF-TOP funding from the University of Antwerp, Belgium. Sincere gratitude to Professor Sophie Cambre from NANOrOPT research group at University of Antwerp for the opportunity to use the Photoluminescence Spectrometer FLS 1000.

High-throughput Photocatalytic Reactor with Operando Characterisation for Fast Screening of Materials for the Photodegradation of Water-Borne Pollutants

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Over the years, many researchers in the field of photocatalysis have employed various batch reactor systems such as petri dishes to screen and study the properties of novel photocatalysts using model pollutants [1]. Subsequently, employ external characterisation techniques such as ultraviolet-visible (UV-vis) spectrophotometric measurements to evaluate the extent of photodegradation as a function of time [2]. Recently, several studies have reported using high-throughput photocatalytic screening approaches to eliminate single sample measurements and permit multiple samples to provide large amounts of data for machine learning algorithms. The systems lack integration of operando optical characterisation, i.e., sample trays needed to be transferred to an absorbance detection instrument– thus limiting the effective throughput [3]. To resolve these limitations, a novel fast-screening photocatalytic reactor system (FaS-PhoReS) using simulated air-mass 1.5 global terrestrial sunlight was demonstrated. The system offers the following advantages: i) it is coupled with a UV-vis-NIR spectrometer and utilizes automated Lab-VIEW software to control and facilitate data measurements and simultaneous recordings, ii) eliminates the need to physically transfer the sample to the spectrophotometer, iii) is capable of processing 32 samples at once, iv) utilises a facile non-contact sensing technique based on optical fibres to detect light signals through the sample during the photodegradation process and v) its vertical geometry for absorbance measurements alleviates any artefacts on measurement accuracy caused by evaporation. The capability, applicability, and repeatability of the system are validated in operando via i) photolysis tests of 12 water-soluble organic dyes to investigate the photostability under simulated sunlight; and ii) photocatalytic degradation of the photostable dyes (identified in the photolysis) – using TiO_2 thin films prepared by atomic layer deposition (ALD). The applicability of the instrument was also demonstrated: i) to work with TiO_2 nano-powders – without the need for stirring; ii) for the in-situ detection of reactive oxygen species. Figure 1 presents an illustration of FaS-PhoReS and the degree of photodegradation of methyl orange (MO) with ALD-TiO_2 thin films after 360 min [5]. It was observed that removal efficiency of 90% with TiO_2 film, while almost zero under photolysis. FaS-PhoReS system exhibits consistent and repeatable results. Thus, FaS-PhoReS demonstrated a new perspective approach to evaluating photocatalytic materials.

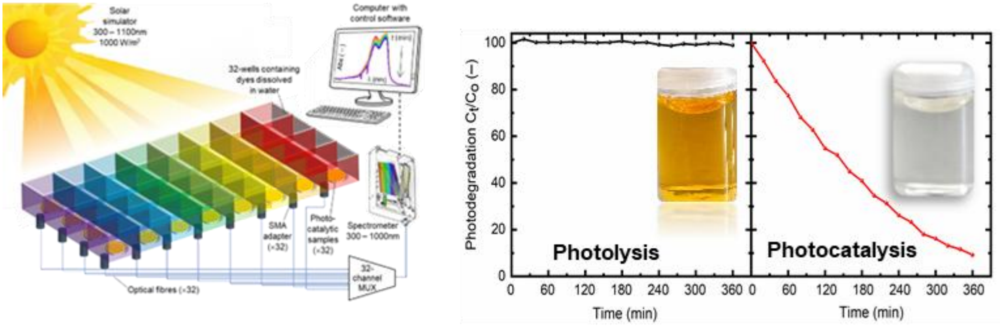

Figure 1. Overview of the FaS-PhoReS and degree of photodegradation without and with TiO_2 thin films.

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This work has received financial support from the DFG "SolPhoWat" project and the Ministry of Science, Research and Arts (MWK) of Baden-Württemberg for funding the SPheRe project.

Black mass from Spent Li-batteries as co-catalyts of C_3N_4 photocatalyst for photoreforming of aqueous solutions of organics

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Nowadays there is a justified enhanced interest in sustainable technologies that integrate different renewable resources. In this context, the development of processes for the valorisation of spent lithium-ion batteries (s-LiBs) is an urgent issue [1]. In the current work graphitic carbon nitride (g-C_3N_4) has been enriched with a metal-based co-catalyst obtained from the mixture of anode and cathode powders (black mass (BM)) contained into s-LiBs (see Figure 1). g-C_3N_4 possesses optimal characteristics as a photocatalyst even under solar irradiation, and its coupling with various materials as graphene [2,3] or TiO_2 [4,5] improve the H_2 productivity by photoreforming. On the other hand, the reuse and valorisation of s-LiBs is an urgent issue [4].

The photoreforming technology is aimed to obtain H_2 from water and simultaneously oxidizing organic molecules to higher added-value substances in the presence of semiconductors as C_3N_4 [2,3]. In this research, BM from s-LIBs, containing mainly Co, and lower amounts of Ni and Mn, has been used pristine or activated along with g- C_3N_4 that was prepared by calcination of melamine, urea, thiourea or dicyanamide. Various sets of composites has been prepared by different strategies to obtain g- C_3N_4/BM photocatalysts with an amount of BM enough to bring to the composite a content of BM in the range 0.5 to 2 % w/w. The obtained materials were tested for H_2 production by photoreforming of aqueous solutions of ethanol, glycerol, triethanolamine or real wastewaters containing organics irradiated with UV light. Photoreactivity tests were performed in the absence or in the presence of 1% Pt.

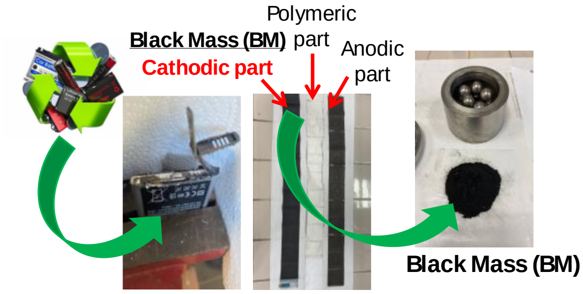

Fig. 1. Spent Li-batteries (s-LiBs) contain Black mass (BM) rich in metals. They can be opened and the content recycled as co-catalysts to prepare composites with g-C3N4. The black mass was ball milled before been used.

The presence of small amount of BM enhanced the carbon nitride activity in photoreforming of aqueous solution of organics. In particular, the best result in terms of H_2 productivity was obtained for the photoreforming of an aqueous solution of ethanol (0.36 M) by using as catalyst g-C_3N_4 with a content of BM-reduced equal to 0.5 % w/w. In the presence of this catalyst, the highest amount of H_2 obtained was 4592 μmol h^{-1} g^{-1}.

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P-90

Photocatalytic removal of organic pollutants in wastewater using a modified hydrochar catalyst

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This work studies the efficiency of a novel photocatalyst, based on hydrochar (HC) modified with hydrozincite (HDZn), in degrading pollutants in wastewater. The HDZn was created using a chemical co-precipitation method involving thermal urea hydrolysis, without any prior activation or calcination. The HC modified with different weight percentages of HDZn (0 - 15 wt%) was synthesized through a hydrothermal process at 300°C in acid medium. These materials were not calcined or thermally treated post-synthesis [1]. The photocatalytic activity of these materials was evaluated based on the photodegradation of metoprolol (5 ppm) and thiacloprid (5 ppm), using UVC radiation and solar light simulator (solarbox). The characterization of this catalysts showed that heterojunctions and oxygen vacancies play a key role in the photodegradation reaction mechanism, reducing the likehood of electron-hole recombination and enhancing the photocatalytic activity. The material with the highest photodegradation efficiency contained 10% hydrozincite by weight (see Figure 1), suggesting that these materials could be a promising option for decomposing pollutants in wastewater. It achieves substantial degradation and mineralization percentages: 94% and 82% for metoprolol and thiacloprid, respectively, using solar light simulator, and, 83% and 72% for metoprolol and thiacloprid, respectively, using UVC light.

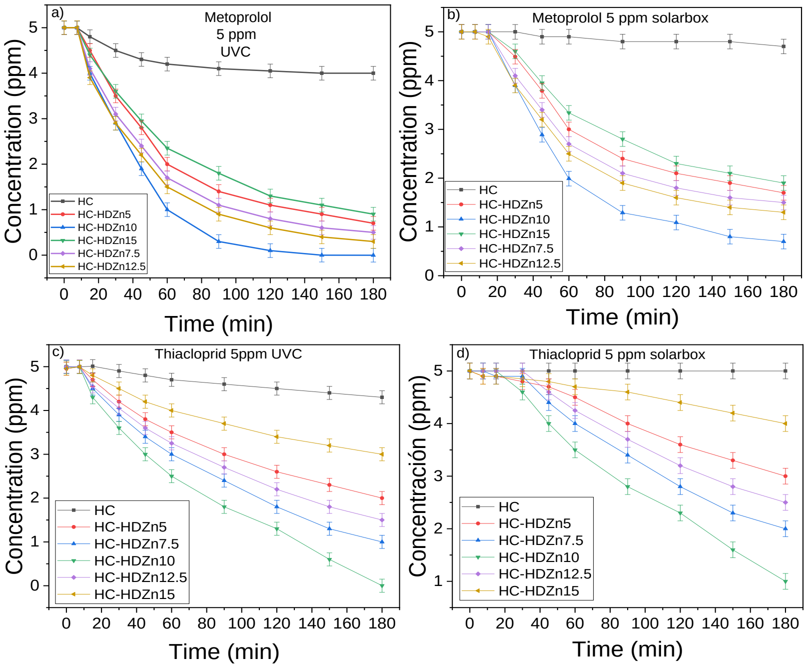

Fig. 1. Concentration profile versus time of photodegradation of pollutants using UVC radiation and solar simulation.

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The authors thank the Secretary of Education, Science, Technology and Innovation (SECTEI) of Mexico City for the contribution of a scholarship for a postdoctoral stay at the Universidad de Barcelona for the development of this manuscript.

Application of Cerium-Based Materials Supported on Different Zeolites for the Photocatalytic Degradation of Methyl Red in Water

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Water contamination due to synthetic dyes from textile, paper, and other industries is a significant environmental concern. These dyes are often highly stable, non-biodegradable, and toxic, posing risks to aquatic ecosystems and human health. Conventional wastewater treatment methods, including physical, chemical, and biological techniques, often fail to achieve complete dye degradation. Therefore, advanced oxidation processes (AOPs), particularly photocatalysis, have gained attention as effective and sustainable solutions for dye removal.

Zeolites have been widely studied for their adsorption and catalytic properties in wastewater treatment. Their high surface area, tuneable pore structure, and ion-exchange capacity make them suitable as catalysts or catalyst supports in photocatalytic applications. Recent studies have reported promising results in zeolite supported CdS/TiO2/CeO2[1] achieving 86% degradation of methylene blue, and CeO2/ NaX in photocatalytic degradation of brilliant green dye[2] and methyl orange degradation of about 95.6%[3]. The integration of CeO2 as photoactive catalyst onto zeolite frameworks has been explored to enhance the efficiency of synthetic dye degradation in watewater. In this context, the main motivation of this work is to evaluate whether it is possible to prepare zeolite-based catalysts with a low cerium content that offer competitive performance in the photocatalytic decomposition of methyl red in water.

Incorporating cerium into zeolites further enhances the photocatalytic degradation of methyl red by improving several key properties. Cerium increases light absorption, enabling more efficient use of visible light. In addition, it acts as an electron trap, reducing charge-carrier recombination and thereby boosting the overall reaction efficiency. Moreover, the combination of cerium and zeolites improves adsorption capacity: the porous structure of the zeolites, combined with cerium's surface characteristics, facilitates the capture of methyl red molecules and promotes their degradation. The synergistic effect of cerium's redox properties and the zeolites' ion-exchange capacity leads to more effective pollutant breakdown, making these materials highly promising for sustainable wastewater treatment (Figure 1).

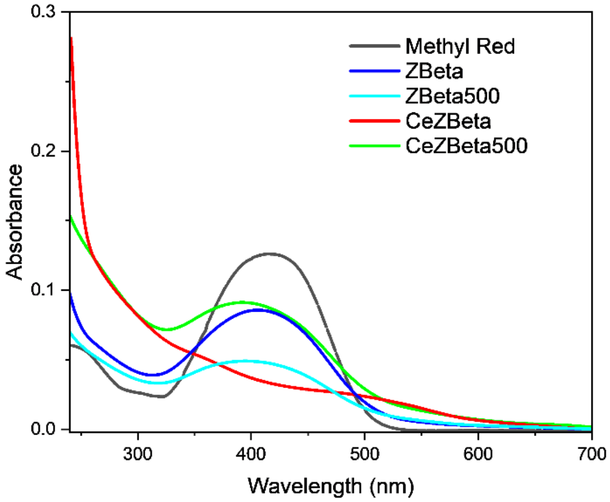

Fig. 1. Photocatalytic degradation of Methyl Red on Cerium-based materials supported on beta zeolite catalysts in aqueous phase after 1h reaction under UV illumination (365 nm).

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Acknowledgements

This work has received financial support from MCIN: TED2021-131914B-I00.

P-92

Fe/Mo bimetallic phases supported on TiO_2 for N_2 reduction into NH_3 by photo-processes

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As climate change and global warming are among the biggest challenges in the coming years, the main objective is to develop and use renewable energy sources like wind, solar and sea water to mitigate their impact. In our modern society, ammonia is considered as an unavoidable commodity chemicals, as well as an ideal H_2 storage and transportable material due to its green and high energy realease capacity. This work consists in the use of solar power to catalytically produce NH_3 with low carbon emission, as the widespread conventional Haber-Bosch process requires so far high temperature and pressure conditions (typically 400°C and 100-200 atm), which is responsible of 300 million tons of CO_2 emission annually. Thereby the low-temperature photocatalytic N_2 fixation/reduction has become a hot topic in the recent years by allowing a green and environmentally-friendly way of production for ammonia using N_2 as cheap abundant reactants and photons as immaterial reactant under far milder and more sustainable conditions than the Haber-Bosch process.

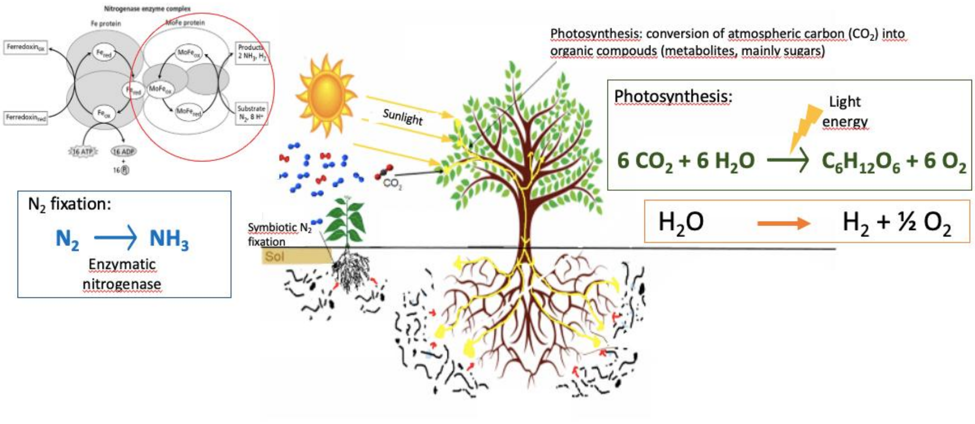
In nature, the nitrogenase enzyme can convert N_2 to NH_3 at ambient conditions. The nitrogenase contains two key proteins, an Fe-based protein and a MoFe-based protein, working in tandem to convert N_2 to NH_3. The Fe-based protein hydrolyses the adenosine triphosphate (ATP) to adenosine diphosphate (ADP), hereby generating electrons that are subsequently transferred to the MoFe-based protein where N_2 is reduced to NH_3. As a consequence, our work is inspired from the natural enzymatic process based on the nitrogenase with MoFe active cluster sites for the development of novel photocatalytic systems for N_2 fixation/reduction to synthesis NH_3 under mild conditions.

This study deals with the assement of both gas-phase photocatalytic and photo-thermal N_2 reduction using either H_2O or H_2 as H provider. Two different complementary methods were used to monitor the NH_3 production, respectively (1) a classical approach using indirect colorimetric tests (indophenol method) after accumulation in liquid phase and (2) a less common method based on direct measurement of gas-phase NH_3 production.

The present presentation will be focused on the elaboration, characterization and photocatalytic evaluation of Fe/Mo bi-metallic TiO_2-supported systems for both photocatalytic and photo-thermal NH_3 production from N_2 reduction. Structure/activity correlation will be discussed tuning the total metal (Fe+Mo) content, the Fe-Mo proportion and the Mo and Fe surface oxidation states.

Acknowledgements

This work has received financial support from the French Ministry of Higher Education and Research for handicap doctoral contract.



P-93

On the growth kinetics of Au/TiO2 Nanowires

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Keywords: growth kinetics; TiO2; Au; Nanowires; heterojunction

One of the emerging challenges in advanced societies is related to the reduction of pollution in water. The supply of safe and clean water will be one of the major issues in the decades to come. Consequently, the development of new, inexpensive, environmentally friendly methodologies and materials for wastewater remediation is desired.

In the present work, we report on the synthesis and properties of Au/TiO2 nanowires (NWs) grown by seed-assisted thermal oxidation [1-4]. NWs are realized by annealing (in air at 750 °C) a thin Au film deposited onto a metallic Ti substrate. The material shows a peculiar structure composed of TiO2 NWs with Au nanoparticles (NPs) on top as shown in Figure 1a. The NWs length is about 1-2 µm while the diameter ranges between 50 and 100 nm. The material is deeply characterised optically, structurally and electrochemically [1,2]. Moreover, it demonstrates remarkable photocatalytic activity in the degradation of water pollutants, which allows it to be profitably used for water remediation [3,4].

Despite the potential use in the environmental remediation field and the research community interest, the growth mechanism of the NWs realized by seed-assisted thermal oxidation is still unclear. Experiments to disclose this mechanism will be presented. We observed that the presence, before the annealing, of a micron-thick TiO2 layer over the Ti substrate, hinders the formation of the NWs. Moreover, the presence of the Au NPs metal is mandatory for the NWs' growth. We investigated in detail the effects of the substrate, the TiO2 thickness and the oxidation time on the formation of the NWs. We identified a possible growth mechanism, involving the Ti interstitials (Ti+) diffusing from the Ti substrate to the Au NPs. This is schematically presented in Figures 1a and 1b. The current-voltage characteristic, measured with a Conductive Atomic Force Microscopy (C-AFM) on a single nanoparticle, evidences the formation of a nanometric heterojunction at the TiO2/AuNP interface (Figure 1c). We speculated that the interface Au/TiO2 attracts the Ti+ interstitials boosting the oxidation rate and leading to the formation of TiO2 NWs.

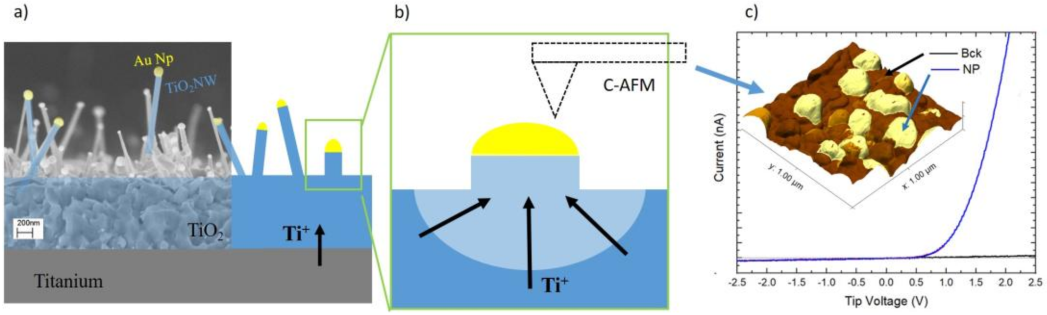

Fig. 1. a) Cross-section SEM image of the TiO2 NWs with Au-Np on top. A schematic representation of the NWs is superimposed to SEM image. The Ti substrate and Ti interstitials (Ti+) diffusing from the Ti substrate to the NWs, are also represented. b) Schematic representation of the Au-Nps/TiO2-Nws. The brighter region represents the depletion layer due to the Au/TiO2 heterojunction. Black arrows indicate the interstitials diffusion. The C-AFM tip is also schematically represented. C) 3D morphology superimposed to the current map (in the inset) and I-V characteristic measured on a single nanoparticle (blue) and the background (black). The rectifying behaviour of the nano-heterojunction is apparent.

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Acknowledgements and Funding

The authors would like to express their sincere gratitude to Giuseppe Pantè (CNR-IMM). This work is partially funded by the European Union (NextGeneration EU), through the MUR-PNRR project SAMOTHRACE (ECS00000022). This Work is also partially funded by Ministero delle Imprese e del Made in Italy (MIMIT) under IPCEI Microelettronica 2, project MicroTech_for_Green.

Development of an air purification prototype based on photocatalytic filters with biocidal activity

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Respiratory diseases are among the top five risks to public health, causing a large number of deaths per year. Airborne transmission is the main vector of spread and the likelihood of infection is much higher at indoor environments. There is a need to develop innovative sanitary technologies that enable safe environments and help providing preventive devices to contain the transmission of infectious diseases. To this end, we propose new air purifiers based on photocatalytic filters that inactivate viruses and bacteria by oxidative stress, inhibiting their ability to infect cells.

Zinc oxide nanoparticles exhibit antimicrobial activity due to the photoproduction of reactive oxygen species (ROS). However, the recombination rate of photogenerated electron-hole pairs decreases their photocatalytic performance [1]. The use of zinc oxide - cerium oxide nanocomposites has been proposed, since the formation of suitable heterojunctions can reduce the charge recombination processes and in addition, CeO_2 also exhibits inherent redox characteristics that can enhance the generation of such ROS. Since the electronic properties of CeO_2 depend on the types of exposed faces [2], the influence of different ceria morphologies on the behaviour of nanocomposites has been analyzed, observing that the heterojunction with ceria nanocubes, presenting highest proportion of exposed (100) faces, results in higher inactivation. Several characterization techniques (TEM, XRD, Raman, DRIFTS, EPR, XPS/UPS, BET, UV-Vis, fluorescence lifetimes) were used to analyze the structure and morphology of these nanocomposites, as well as their optoelectronic properties. Viral titration assays to evaluate the antiviral effect, as well as inactivation tests of both Gram-positive and Gram-negative bacteria, were performed. Different assays have been designed to elucidate the photocatalytic mechanism and the inactivation process.

In addition, the actual viability of viruses in aerosols has been assessed in a specifically designed chamber. It allows the generation of bioaerosols with viral load, real-time *in situ* monitoring of suspended particles and sampling of bioaerosols, which makes it a powerful tool to study the efficiency of air purification systems. A prototype of the air purifier has been built and tested inside the chamber, using a filter with the most active photocatalyst, obtaining very promising results such as a drop of 7 logarithmic units in the concentration of viruses with infective capacity in the aerosol, and 3 logarithmic units in the viruses physically retained in the filter (Fig. 1c).

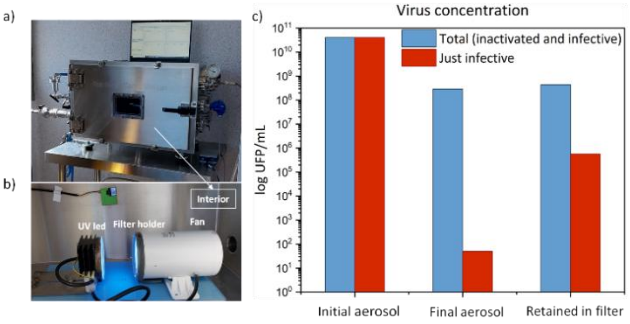

Fig. 1. a) Aerosol chamber (CORINA). b) Interior of CORINA with the photocatalytic air purifier prototype. Inside CORINA, a stable aerosol containing viral load was generated. The aerosol was recirculated through the illuminated photocatalytic filter and subsequently both the virus retained in the filter and the portion remaining in the air or aerosol were analyzed. c) Results of airborne inactivation against phi29: both the concentration of viruses that can continue to infect by viral titration and the total concentration of virus (with and without infective capacity) were analyzed by RT-qPCR.

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Acknowledgements

Project funded by “la Caixa” Foundation, code LCF/PR/HR22/52420032, HR22-00813 and by CSIC PTI+ Salud Global, Nextgeneration EU.

Scaling up Solar Hydrogen Production: Material Innovations and Reactor Design Strategies

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The accelerating global pursuit of clean energy has spotlighted solar-driven hydrogen production as a key pathway toward sustainable fuel alternatives. Among various approaches, photocatalytic water splitting and/or wastewater treatment with simultaneous hydrogen production using solar energy presents a highly promising yet technically challenging solution due to issues related to efficiency, material stability, and scalability.

This study investigates solar-driven hydrogen production by leveraging advanced photocatalyst systems—modified Cadmium Sulfide (CdS) and Covalent Organic Frameworks (COFs)—in conjunction with innovative solar reactor designs that enhance light harvesting and process scalability. While CdS and COFs offer suitable band gaps for visible light absorption, their broader application is limited by photocorrosion, reduced stability, and environmental concerns.

To overcome these constraints, this research introduces material innovations such as CdZnS composites (via ZnS modification of CdS) and COF/g-C_3N_4 hybrids, which exhibit improved charge separation and suppressed electron-hole recombination. Crucially, the study integrates these materials into a semi-pilot-scale solar reactor system (see Fig.1), engineered to maximize solar photon utilization through optimized geometry, enhanced light-material interaction, and uniform light distribution across the photocatalytic surfaces. The impact of several critical parameters on photocatalytic hydrogen production was systematically studied. These include catalyst type, light intensity and wavelength, concentrations of catalyst and co-catalyst (platinum nanoparticles), electron donor concentration (ascorbic acid), and flow rate. Optimization of these variables in both batch and flow systems led to a significant improvement in hydrogen evolution rates and long-term operational stability under real sunlight conditions. An example of the effect of light intensity and catalyst concentration is illustrated in Fig. 1 (b) Furthermore, a comparative evaluation of batch versus continuous-flow operation modes was investigated. While batch reactors are simpler and ideal for initial screening, continuous flow reactors offer superior scalability, improved photon utilization, and consistent reactant exposure, making them more suitable for long-term solar applications.

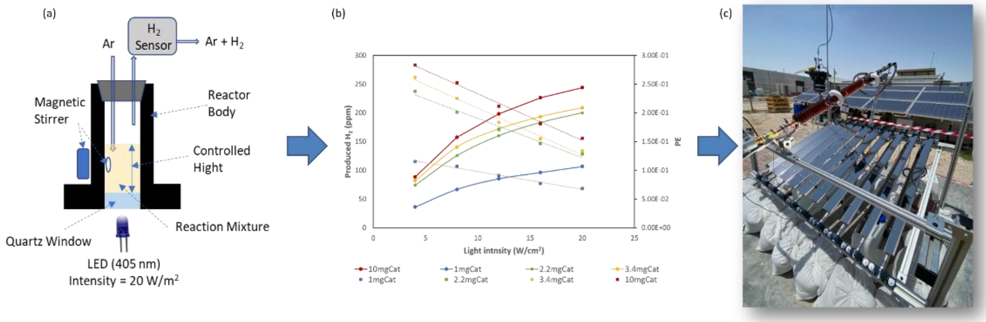

Fig. 1. Scaling up solar hydrogen production unit.

Experimental findings from both lab-scale and solar reactor trials reveal notable improvements in hydrogen evolution rates and operational stability in the lab using artificial light sources as well as under real sunlight conditions. These results underscore the synergistic role of material engineering and solar reactor design in advancing solar-to-hydrogen energy conversion. This work contributes actionable insights toward the practical deployment of solar-integrated photocatalytic systems for green hydrogen production.

Acknowledgements
This work has received financial support from Shell Qatar.

Comparison of binders in terms of activity and stability of Pt/TiO₂ photocatalyst films for green hydrogen production

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Photocatalytic water splitting to produce green hydrogen $\left(2H_2O \xrightarrow{h\nu,cat.} 2H_2 + O_2\right)$ is a possible answer to the energy and climate problems. Various groups are working on the development of catalysts to make better use of sunlight and increase catalytic activity for this reaction. However, immobilization of the photocatalyst is essential for large-scale application, and the choice of immobilization method is crucial for the activity and stability of the photocatalytic film.

In this contribution, the titanium dioxide (TiO_2) modification PC500 was used as a photocatalyst and decorated with platinum (Pt) nanoparticles by photodeposition, because $Pt@TiO_{2,\ PC500}$ shows a very high activity for water reduction using ethanol as the sacrificial agent [1]. The photocatalyst was immobilized on stainless steel plates (3 cm x 3 cm) by various methods including electrophoretic deposition (EPD, no binder), drop coating with Nafion or polyhydroxyalkanoate (PHA) as organic binders (polymers), and the sol-gel method (SiO_2 as the binder). In addition, the photocatalyst was immobilized on a filter paper using cellulose (biopolymer). PHA and cellulose have been already tested as possible binders for the immobilization of photocatalysts [2,3].

The activity of the photocatalytic films was measured in a top irradiation setup (365 nm UV-LED) (Figure 1, left) and gas phase composition after 1 h irradiation was determined by gas chromatography. The film stability was determined by recycling test, measuring the weight loss after individual runs.

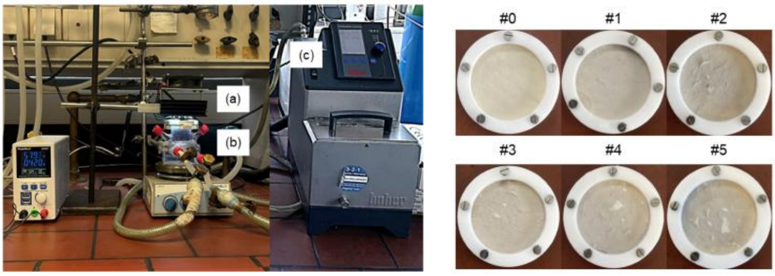

Figure 1: Setup for photocatalytic measurements (a: photoreactor, b: UV-LED, and c: thermostat) (left) and cellulose-immobilized $Pt/TiO_{2,\ PC500}$ (before, #0) and after recycling test (#1-#5) (right).

The main objective was to compare the different immobilizations methods for the same photocatalyst, varying not only the immobilization method but also the ratio of binder to photocatalyst. The quality of the films and the performance of the photocatalysts vary with the method and amount of binder. EPD produces homogenous films but the activity (less photocatalyst) and stability of the film is lower compared to the other methods. The activity decreases when the ratio of binder to catalyst is increased, which was observed in particular with the sol-gel method. Too much SiO_2 in the film reduces the light accessibility of the photocatalyst and thus the activity. With Nafion and PHA, the photocatalytic activity is also lower at higher binder concentrations, but the effects are less than with the sol-gel method. In addition, the different hydrophobicity of the two polymers seems to play a role, as a binder that is too hydrophobic prevents water adsorption on the photocatalyst. The least effect on activity was observed with cellulose, but the stability of the films is not good (Figure 1, right), as already known [2].

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Acknowledgements

The authors acknowledge the funding from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy—EXC 2008/1 (UniSysCat)—390540038.

P-97

Evaluation of Ga_2O_3–TiO_2 heterojunction photocatalysts for water treatment

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Aquaculture is projected to become one of the world's most important food production sectors. Nevertheless, it has been anticipated that aquaculture production could decrease in the future owing to some challenges and major constraints such as the availability of quality water [1] and the biosecurity of wastewater discharge [2].

Concerning wastewater treatments, one of the available strategies is heterojunction photocatalyst. Heterojunction structures are proven to be extremely efficient for the preparation of advanced photocatalysts due to their feasibility and effectiveness in spatial separation of the photogenerated electron-hole pairs. Several have demonstrated encouraging performance in photocatalysis, such as TiO_2/NiO, BP/g-C_3N_4, CdS/Cu_2O, among others [3].

In this context, gallium oxide (Ga_2O_3) has emerged as a promising material, offering higher redox capabilities and longer-term stability than conventional titanium dioxide (TiO_2) [4]. Although TiO_2 has been the dominant photocatalyst due to its high efficiency, strong oxidation power, low cost, environmental benignity, and excellent chemical and photochemical stability [5], the formation of a Ga_2O_3–TiO_2 heterojunction has been proposed as a strategy to further enhance photocatalytic performance. For instance, it has shown improved efficiency in the photocatalytic degradation of toluene [6].

This study aims to investigate the photocatalytic performance of Ga_2O_3–TiO_2 heterojunctions with varying composition ratios under UV-A irradiation, targeting water treatment applications. This work is part of a broader effort to evaluate efficient photocatalytic materials tailored to aquaculture contexts. Here, we present preliminary results on the inactivation of *Enterococcus faecalis*, a biological indicator of fecal contamination. Future stages of this research will include the evaluation of tetracycline degradation, a contaminant of emerging concern (CEC), as well as testing under real aquaculture water matrices.

Experiments were conducted in a 100 mL batch reactor system equipped with continuous magnetic stirring over 120 minutes, both in the presence and absence of UV-A irradiation (λ = 365 nm). The photocatalysts evaluated included pure Ga_2O_3 and TiO_2 (both at 0.1 g/L), along with Ga_2O_3–TiO_2 heterojunctions synthesized in 50:50, 30:70, and 70:30 mass ratios. *E.faecalis* inactivation was quantified through colony-forming unit (CFU) counts. Tetracycline removal will be analysed using an Agilent 1100 series High-Performance Liquid Chromatography (HPLC) system.

Preliminary results indicate that the photocatalytic process significantly enhanced the inactivation of *E.faecalis* compared to dark conditions. The highest disinfection was observed with pure TiO_2, achieving a 3.55 log reduction at 30 minutes (3,95 log reduction at 120 minutes), followed closely by the Ga_2O_3–TiO_2 heterojunction with a 70:30 ratio, which reached a 3.94 log reduction at the end of the treatment. The 50:50 and 30:70 heterostructures showed log reductions of 3.59 and 0.93, respectively, while pure Ga_2O_3 achieved a 2.05 log reduction. In contrast, under dark conditions, inactivation was minimal across all materials, with log reductions not exceeding 0.88.

These results confirm the potential of heterojunction photocatalysst in pathogen inactivation and highlight that although the 70:30 heterostructure shows promising efficiency, not all heterojunctions outperform the individual materials. This suggests that photocatalytic activity strongly depends on the composition and interfacial characteristics of the heterostructure. Therefore, further exploration of Ga_2O_3–TiO_2 heterojunctions is needed—focusing on understanding charge transfer mechanisms, optimizing material ratios or synthesis methodology, and testing under real aquaculture water conditions— to guide their development as effective photocatalysts for aquaculture water treatment applications.

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Acknowledgements

This work has received financial support from Spanish MCIN/AEI/10.13039/501100011033.

Design of TiO_2 monolithic ceramic photocatalyst for water purification

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[a] National Institute of Advanced Industrial Science and Technology
[b] Chiba Institute of Technology
[c] Photocatalytic Materials Incorporated

Despite extensive research on photocatalytic water purification, practical applications remain scarce. One major challenge is the lack of durable photocatalytic materials that can function in water over long periods. However, the demand for photocatalytic water treatment is significant, particularly for drinking water purification using sunlight in developing countries. To meet this need, it is essential to develop photocatalytic materials that are as maintenance-free as possible, safe, and capable of long-term use.

To address this issue, we have developed a TiO_2 monolithic ceramic photocatalyst composed solely of TiO_2, which exhibits high durability for long-term application. Here, economic feasibility is a crucial consideration, especially for use in developing countries. While TiO_2 is an inexpensive material, its photocatalytic function depends on light exposure. Non-functional areas (i.e., existence of shadow area) reduce economic efficiency. Therefore, we designed a photocatalyst configuration in which thin, brick-shaped TiO_2 ceramic pieces are enclosed within a glass tube and connected in series. This design ensures uniform light exposure from all directions, assuming implementation in a parabolic trough (PTR) or compound parabolic concentrator (CPC) system, thereby minimizing shadowing effects. For the synthesis of photocatalyst ceramic, we used a commercially available titania sol derived from titanium alkoxide. To enhance viscosity and introduce porosity, the sol was mixed with cellulose, forming a precursor sol. This sol was then injected into molds cut by CNC machining based on 3D-CAD designs from calcium silicate, gypsum, and terracotta ceramic plates. After drying, the gel was calcined and a TiO_2 ceramic photocatalyst was obtained. The crystal transition temperatures of TiO_2 for each mold were analyzed using XRD and TG/DTA. The resulting TiO_2 ceramics were packed into glass tubes (Fig. 1), and their catalytic activity was evaluated by measuring the photocatalytic degradation rate of 1 mM formic acid in a closed-circuit reactor irradiated by UV-LED light (λ = 365 nm) from all directions (Fig 2).

XRD and TG/DTA analyses indicated that TiO_2 crystallizes from its amorphous state into anatase at approximately 400°C. Low-temperature calcined TiO_2 was highly porous, and this structure is good for high activity. However, it became fragile due to water-induced swelling in its porous structure in a water phase. To balance mechanical robustness and photocatalytic performance, we determined that calcining at a temperature slightly below the anatase to rutile transition despite a decrease of specific surface area results in an optimal photocatalytic material with both durability and high activity. The catalyst weight did not decrease but rather slightly increased after 6 months of continuous 200 mL/min tap water flow test. The ceramic catalyst was not degraded at all by the water flow, and this is thought to be due to impurities in the tap water remaining on the catalyst surface.

Fig. 1. Brick-shaped TiO_2 ceramic monolithic photocatalyst in a Glass-tube.

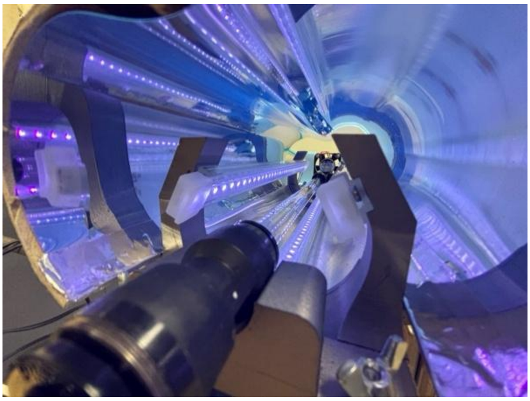

Fig. 2. UV-LED closed-circuit photocatalytic reactor

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This work has received financial support by Scientific Research (B) 22H03773 from the Japan Society, and Innovation inspired by Nature Research Support Program, SEKISUI CHEMICAL CO. LTD.

P-99

Enhanced adsorption ability and photocatalytic efficiency of supported layered double hydroxides

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Layered double hydroxides (LDHs) are an emerging class of two-dimensional (2D) layered materials from the family of hydrotalcite-like compounds. The structure of LDHs is also described based on the stacking of charged brucite-like layers [1]. LDHs are represented by the general formula of $[M^{2+}{}_{1-x}M^{3+}{}_{x}\ (OH)_2]^{x+}\ [A^{n-}{}_{x/n}.mH_2O]^{x-}$ where M^{2+} and M^{3+} are divalent and trivalent metal cations while A^{n-} is an exchangeable interlayer anion of valence n (Fig. 1). The structural features of LDHs can be tailored by tuning the types of M^{2+} (e.g. Mg^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+} etc.) and M^{3+} (e.g. Al^{3+}, Fe^{3+}, Cr^{3+}, Co^{3+} etc.), the molar ratio of M^{2+}/M^{3+}, the nature of interlayer anions (e.g. NO^{3-}, Cl^-, $CO_3{}^{2-}$, $SO_4{}^{2-}$ etc.) and preparation temperature to meet the requirements for the application areas [2]. The interlayer distance (basal spacing) in LDH structure is influenced by the ionic radius, charge density, and electronegativity of metal cations, as well as the nature of the interlayer anions. LDHs can be considered suitable adsorbent materials to host various guest molecules between the layers [3]. This enables the formation of probable interactions, such as electrostatic attraction and hydrogen bonding with the target molecules.

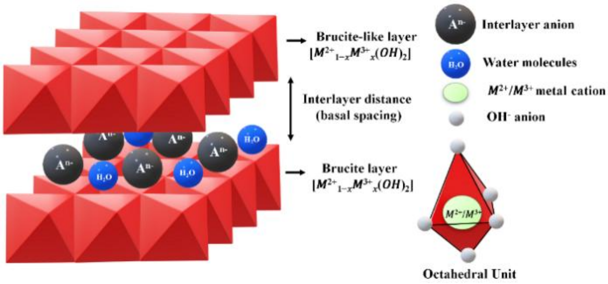

Fig. 1. LDH structure.

LDHs are transformed into layered double oxides (LDOs) upon thermal treatment at and above 500°C. The decomposition of the layered structure of LDHs by calcination initiates the formation of mixed metal oxides. The photoactivity of LDOs is attributed to the formation of photoinduced defects on the surface oxides, which can act as active centers for surface reactions. It is also noted that LDOs exhibit improved photoactivity for dye degradation compared to LDHs, owing to the formation of mixed metal oxides such as ZnO and Fe2O3, based on the nature of the metal cations in the structure. Despite the excellent properties of LDHs and LDOs in adsorption and photocatalytic processes, there are still drawbacks that limit their practical application. In this study, a supported catalyst system (M^{2+}/M^{3+}-Support) is prepared. Zeolitic structures are utilized as support materials in the matrix. The structural properties of the as-prepared catalysts are examined using XRD, SEM and BET analysis. Thereafter, their adsorption abilities in the dark and photocatalytic performances under UV irradiation are evaluated in the degradation processes of probe molecule(s).

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This work has received financial support from the Boğaziçi University Research Foundation (Project No. BAP 22BD8/19362).

P-100

Junctions, Charge Transfer Energetics, and Surface Recombination Sites Control Energy Conversion with a Gallium Phosphide Photocatalyst for Hydrogen Evolution

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Gallium phosphide is a well-established photoelectrode material for H_2 or O_2 evolution from water, but particle-based GaP photocatalysts for hydrogen evolution are very rare. To understand the reasons, we investigated the photocatalytic H_2 evolution reaction (HER) of suspended n-type GaP particles with iodide, sulfite, ferricyanide, ferrous ion, and hydrosulfide as sacrificial electron donors, and using Pt, $RhyCr_{2-y}O_3$, and Ni_2P HER cocatalysts.

A record AQE of 14.8% at 525 nm was achieved after removing charge trapping states from the GaP surface, adding a Ni_2P cocatalyst to reduce the proton reduction overpotential, lowering the Schottky-barriers at the GaP-cocatalyst and GaP-liquid interfaces, and adjusting the electrochemical potential of the electron donor. The work showcases the main factors that control charge separation in suspended photocatalysts, and it explains why most known HER photocatalysts in the literature are based on n-type and not p-type semiconductors.

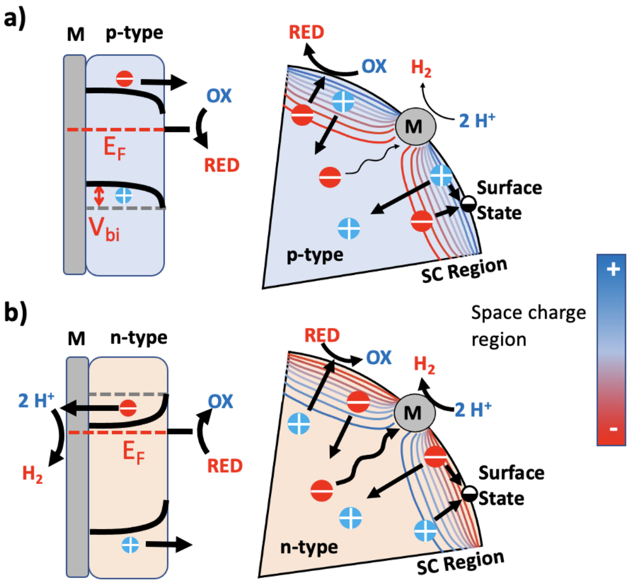

Fig. 1. Band bending in a) p-GaP and b) n-type GaP photocatalyst at the semiconductor-cocatalyst (M) and semiconductor-liquid interfaces and corresponding charge separation under illumination.

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This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Science under award number DE-SC0015329. The Kratos Supra XPS instrument was funded through the US National Science Foundation under award DMR-1828238.

P-101

Highly fluorinated g-C_3N_4 for photocatalytic applications

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Graphitic carbon nitride (g-C_3N_4) has been investigated in the past years as an organic photocatalyst for potential application such as remediation (organics degradation), CO_2 artificial photosynthesis and for water splitting under light irradiation [1]. However, its applications are limited due to low utilization of the visible solar energy, low specific surface area and high recombination of photogenerated electron-hole pairs [2]. Therefore, carbonitride-based nanocomposites with engineered heterojunction and/or doping of g-C_3N_4 with elements such as B, C, N, O and F have been investigated. Few studies focused on the fluorination of g-C_3N_4 and with limited doping using mainly hydrothermal methods with F- (via NH4F or analogues) [3]. Recently, L. Sun et al have explored the F_2 (diluted) gas approach to prepare fluorinated g-C3N4 (F content of 7.05 at. %) with drastic structural distortion due to transformation of sp2 hybridization carbon atoms to sp3 and enrichment of nitrogen defects [4]. It results with the improvement of absorption in the visible range and of the photocatalytic performance.

In order to extend the fluorination content and to investigate the resulting photocatalytic properties, carbonitride-base materials were fluorinated with pure F_2 gas at room temperature. The pristine materials were defective carbonitrides (CN and CNO) prepared from melamine decomposition and a g-C_3N_4 nanocomposites embedding carbon nanodomains (CCN) derived from the melamine/carboxylic adduct route [5]. The resulting highly fluorinated materials (F/C at ratio up to 0.96), after stabilization due to their explosive character, were characterized by a large panel of techniques such as X-Ray Diffraction, FTIR, XPS, diffuse reflectance spectroscopy (DRS), EPR in dark and visible mode and thermogravimetry analysis coupled with mass-spectroscopy (TG-MS). The photocatalytic properties of fluorinated materials were explored by studying the photodegradation kinetics of methyl orange using a Xe lamp. A significantly higher kinetics of degradation was observed for all fluorinated materials compared to their pristine counterpart.

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Influence of different antioxidants on the properties of photoactive starch based TiO2 nanocomposites

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Plastic packaging waste is increasingly threatening the environment due to the still insufficient recycling policies and to the fact that production still relies mainly on fossil sources. Starch is a promising alternative in this regard, as it is an abundant natural polymer possibly deriving from low cost, renewable, and biodegradable agri-food wastes [1]. However, starch is water sensitive, lacks mechanical resistance, and undergoes degradation at relatively low temperature. Introducing TiO2 as nanofiller in starch based nanocomposites is not only a viable way to increase mechanical stability, but also to endow the final material with photo-induced properties. Moreover, the addition of antioxidant molecules of natural origin has been proposed to prevent microbial growth or oxidative damages, thus extending the shelf life of the packaged food products. However, often natural extracts or essential oils from plants like rosemary [2], containing a huge variety of antioxidant molecules, have been used to this aim, thus limiting the knowledge on the interaction of these compounds with the starch matrix at a molecular level.

In the present contribution, starch based nanocomposites containing three different antioxidants (cinnamic acid, caffeic acid, and ferulic acid), TiO2 as the nanofiller, and glycerol as the plasticizer, have been produced by a simple casting method in the form of films. The films have been characterized by solid state NMR, IR, UV-vis spectroscopies, and X-ray diffraction. Out of the three antioxidants investigated, caffeic acid introduces a certain degree of crystallinity in the starch matrix. Moreover, due to the strong electronic coupling of caffeic acid with the surface of TiO2, the nanocomposites containing caffeic acid show the highest stability under irradiation, limiting the light induced formation of CO2 and displaying the highest antioxidant ability.

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This work has received financial support by the European Union – Next Generation EU, Mission 4 Component 2 - CUP E53D23009110006.

P-103

Preparation and Characterization of Photocatalytically Active g-C_3N_4 Coatings with Camphor-Induced Porosity for the Efficient Degradation of Antibiotic Pollutants

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Graphitic carbon nitride (g-C_3N_4) is a promising metal-free semiconductor consisting of carbon and nitrogen elements. This gives it clear advantages over other metal-based photocatalysts. The material has a narrow band gap (2.7 eV), good stability, and its structure and properties can be easily modified [1]. This has attracted increasing attention in recent years in the field of photocatalysis. It has also been successfully applied in hydrogen production from water, CO_2 reduction, and the degradation of organic pollutants. Its synthesis is simple and cost-effective. It is typically prepared via thermal condensation of nitrogen-rich precursors such as melamine or urea.

The advantages of g-C_3N_4 include the availability of basic elements (carbon and nitrogen), easy synthesis, and the potential for large-scale production. Despite these benefits, bulk g-C_3N_4 exhibits several limitations: low specific surface area, limited absorption in the visible light range, and a high recombination rate of photogenerated charge carriers. However, these drawbacks can be effectively mitigated through various modification strategies [2].

By introducing porosity into photocatalytic coatings, it is possible to achieve higher effectiveness thanks to better light absorption, larger surface exposure, improved transport processes, and stronger structural support. Thanks to the shortened migration paths of charge carriers, electrons and holes in porous materials can reach the surface more easily, minimizing their recombination and increasing quantum efficiency [3][4].

This study focuses on the development and characterization of visible-light-activated photocatalytic coatings based on graphitic carbon nitride (g-C_3N_4) with an integrated porous structure. The porosity was achieved using camphor as a porogenic agent, which was removed from the structure through sublimation. The resulting thin films were applied to substrates using various techniques. Analytical methods such as SEM, XPS, FTIR, and UV-VIS confirmed their structural and chemical integrity. Subsequently, the efficiency of a selected porous sample was compared to that of a compact one in the degradation of tetracycline in a photomicroreactor. The results demonstrate that improved photon accessibility to the active surface of coatings with macroporous morphology leads to an increased oxidation rate, representing a significant contribution to the treatment of water contaminated with pharmaceuticals.

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This work has received financial support from the Czech Science Foundation through project 23-06843S.

P-104

Photooxidation of As(III) in aqueous solution by heteropolyacid-modified natural ilmenite

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Ilmenite ($FeTiO_3$) has been studied as semiconductor photocatalyst for removing different contaminants from water using visible light, due to its bandgap (E_g = 2.5-2.9 eV) [1]. However, phenomenon such as electron-hole recombination could significantly reduce the efficiency of photocatalytic processes. To address this drawback, heteropolyacids (HPAs) have been supported on the surface of semiconductor materials, acting as a trap for photoexcited electrons [2].

On the other hand, the removal of arsenic species from water sources has special relevance due to their serious implications on human health. Specifically, As(III) species can be 60 to 100 times more toxic than As(V) species, and usually, conventional treatment techniques are less efficient at degrading As(III) compared to As(V). Consequently, arsenic removal processes often imply the oxidation of As(III) to As(V), followed by adsorption or precipitation of the less toxic As(V) [3].

In this work, phosphotungstic acid (PTA) was supported on natural ilmenite, through a wet impregnation process [4]. The effect of the nominal weight ratio PTA/ilmenite (0.2/1.0, 0.3/1.0 and 0.4/1.0) on the impregnation efficiency was analysed by UV-Vis spectroscopy and AAS. It was established that above 0.3/1.0 a supersaturation of PTA in the medium affects the stability of phosphotungstic anions and leads to low impregnation efficiency. SEM micrographs showed random dispersion of the PTA anions on the surface ilmenite. Zeta potential tests showed that, after impregnation, the surface of the materials had a negative charge.

The photocatalytic performance of the materials under visible light showed that the modification allowed an increase in the oxidation efficiency of As(III) to As(V) between 1.6 and 2.6 times. In addition, adsorption studies revealed the high renewal capacity of the adsorption sites on the surface of the obtained materials. Finally, the photocurrent response of the materials shows the ability of PTA anions to act as electron cages and their impact on enhancing electron-hole pair separation.

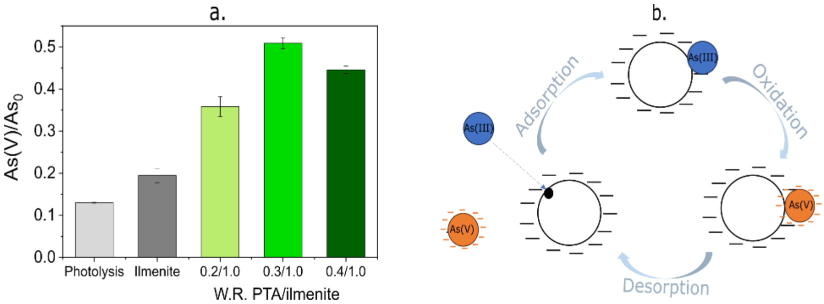

Fig. 1. a. As(III) oxidation to As(V) after 1 h of illumination; **b.** Adsorption/photooxidation/desorption cycle of the obtained materials.

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Acknowledgements

This work has received financial support from Universidad Industrial de Santander and Ministerio de Ciencia, Tecnología e Innovación (Colombia).

Photocatalytic conversion of CO_2 in water by alkali-treated natural ilmenite

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The interest in mitigating green-house gas emissions, such as carbon dioxide, associated with the use of fossil fuels has increased significantly over the last years. Nonetheless, the photoreduction of CO_2 is challenging due to the high stability of this molecule, which requires considerable energy input to break its bonds. Thereby, new alternatives have been evaluated as possible strategies that could lead to obtaining valuable products from contaminating emissions by means of renewable technologies [1]. The photocatalytic conversion of CO_2 has emerged as a feasible and sustainable strategy for simultaneously addressing environmental and energetic issues, considering that solar fuels can be obtained as products [2]. In this regard, the semiconductor photocatalyst plays a crucial role to assure the efficiency of the process. Bearing in mind that CO_2 is an acidic molecule and must be adsorbed on the photocatalyst surface, alkali treatment of the semiconductor has been proposed as an alternative modification for improving the affinity towards CO_2 [3, 4]. Recently, our research group has thoroughly explored the use of natural ilmenite ($FeTiO_3$) as photocatalyst due to its optical, photophysical and electronic properties, and its photo-oxidative and photo-reductive capabilities have been proven [5-7].

In this work, natural ilmenite obtained from a Colombian black sand deposit was modified by impregnation with hydroxides (NaOH, KOH) and carbonates (Na_2CO_3, K_2CO_3) in aqueous solution, using different concentrations (1.0, 3.0, 5.0 wt.%). Zeta potential measurements and proton affinity distributions allowed to identify the modification on the surface hydroxyl groups induced by the alkali treatment. These results were confirmed by FTIR spectroscopy, which also evidenced the presence of carbonate and bicarbonate ions in the materials obtained using carbonate solutions. Na-O and K-O binding in modified materials were evidenced by Na 1s, K 2p and O 1s XPS HR spectra. CO_2 physisorption curves showed the improvement on CO_2 adsorption capability after alkali treatment given by the increasing on hydroxylation grade and/or carbonate and bicarbonates ions added on the surface. Photocatalytic tests were carried out on ultrapure water and acetaldehyde (m/z=45) and methanol ions (m/z=76 and m/z=77) were identified by MS when NaOH at 1.0 wt.% and 5.0 wt.% and Na_2CO_3 at 5.0 wt.% were used. In those materials, it was also evidenced a band gap displacement which could infer the presence of additional energy levels that could avoid electron-hole recombination and favour the formation of carbon products.

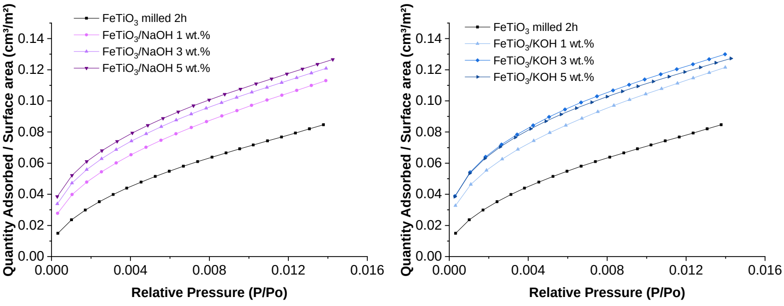

Fig. 1. CO_2 physisorption curves of bare $FeTiO_3$ and treated with NaOH and KOH.

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This work has received financial support from Universidad Industrial de Santander and Ministerio de Ciencia, Tecnología e Innovación (Colombia).

P-106

Electrochemically synthesized copper-tungsten oxides as photo-cathodes for photo-electrochemical water splitting

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Photoelectrochemical water splitting to generate hydrogen using semiconductor nanomaterials is a green technology which could fulfil the growing energy need of the future. Tungsten oxide has received considerable attention in photo-assisted water splitting due to its great advantages such as absorbance in visible region and stability in acidic and oxidative conditions. Electrochemical modification of titanium and tungsten oxides with copper oxide has been proposed as a facile route to produce photo-cathodes for hydrogen evolution under visible light [1-4].

In the present paper, preparation and characterization of photo-cathodes based on copper-tungsten oxides is reported. Briefly, porous tungsten oxide was synthesized via anodization in sulfate-fluoride electrolytes at constant voltage (60 V) and different process durations (2-4 h) followed by thermal treatment at 500 °C. Doping of tungsten oxide with copper oxide was performed via potentiostatic electrodeposition at different negative potentials (-0.2…-0.4 V) in 0.04 M $CuSO_4$+3 M $CH_3CH(OH)COOH$ with a pH of 9.00±0.1 at 60°C. The thickness and in-depth elemental composition of the studied modified oxides was estimated via Glow-Discharge Optical Emission Spectroscopy. Phase composition of the oxides was characterized by X-ray diffraction and Raman spectroscopy, whereas surface chemical composition – with XPS. Electronic properties of the oxides were estimated using high-frequency capacitance - potential measurements in 0.1 M KNO_3. The results are interpreted by contemporary models for the semiconductor/electrolyte junction. Spectral characteristics of modulated photocurrent are also registered to estimate the optical band gap of oxides. Photo-induced carrier dynamics in the oxides was assessed by intensity modulated photocurrent spectroscopy (IMPS) (Fig. 1). Electrochemical impedance spectroscopy was employed to study the ionic and electronic processes in the same electrolyte in a wide range of potentials. Based on the multi-method characterization, conclusions are drawn on the photo-absorbing and photo-catalytic properties of the anodic oxides depending on anodization and copper oxide electrodeposition conditions.

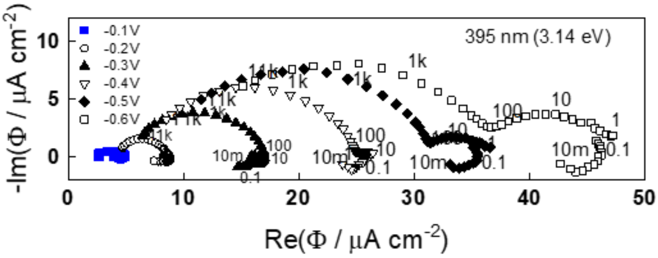

Fig. 1. Intensity modulated photocurrent spectra in 0.1M KNO_3 at light energy of 3.14 eV (395 nm) for a range of applied potentials (-0.1…-0.6 V) , of photo-cathodes obtained by anodic oxidation of W (60 V / 4 h), thermal treatment at 500 °C, and copper oxide electrodeposition at -0.3 V for 0.5 h at 60 °C. Parameter is frequency in Hz.

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Plasma activated water combined with solar disinfection and UVC in the *Enterococcus faecalis* inactivation

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Access to safe and sustainable sanitation is a critical global challenge. Among emerging treatments , plasma-activated water (PAW) have gained attention for its potential to inactivate microbial contaminants without the need for complex infrastructure. PAW is produced by exposing water to non-thermal plasma, generating a rich mixture of reactive oxygen and nitrogen species (RONS) with antimicrobial properties. The antimicrobial effect of the PAW can be increased with different radiation sources like solar disinfection (SODIS) or UV-C. Both radiations uses different range of UV radiation to damage microbial DNA, offering a low-cost, energy-efficient disinfection approach. While each of the three disinfection procedure have shown promise individually, their combined application remains underexplored. This study investigates the synergistic effect of PAW SODIS and UV-C in the inactivation of *Enterococcus faecalis*, a common fecal indicator bacterium and known pathogen, in wastewater. Understanding the interaction between PAW-generated RONS and the additional radiation could lead to the development of more efficient hybrid disinfection strategies. The goal is to enhance microbial reduction while maintaining the sustainability and affordability of the treatment process. This work contributes to the ongoing search for innovative, low-cost solutions for water safety and public health protection in resource-limited environments.

Plasma activated water is produced with a low consumption spark jet discharge above the water surface. The treatment times are for 1 hour with a treated volume of 1 litre. Different aqueous matrices have been evaluated, like deionized (DPAW) or tap water (TPAW). Solar radiation have been generated in a solar chamber from brand *HERAEUS* and UVC was generated with a lamp Philips TUV 6W G6T5, with an irradiance in the sample of 1,1 W/m^2. *E. faecalis* was evaluated with the plate recount method with Slanetz-Bartley as a culture medium, and 48 hours at 36ºC in the incubation chamber.

In this work different proportions and of activated water (DPAW and TPAW) have been evaluated in combination of solar radiation and UVC radiation doses. In **Figure 2**A, the interaction between solar radiation and DPAW is shown, as it can be seen, the presence of both agents reduces treatment time for more than 30 minutes. As it can be seen in **Figure 2**B the efficiency evolution of the DPAW along the time and longer times of storage of the DPAW does not affect the efficiency of the treatment, but reduces the treatment required time. In **Figure 2**C, the influence of the different doses of DPAW in the treatment is shown, as it can be seen the best doses conditions are with a dose of 50 % DPAW. When UVC is added, the treatment times required is reduced to less than 5 minutes.

Although the results achieved with PAW are promising, combining it with different types of radiation significantly enhances the antimicrobial capacity of the water, while also ensuring that no bacterial regrowth occurs in the PAW matrix.

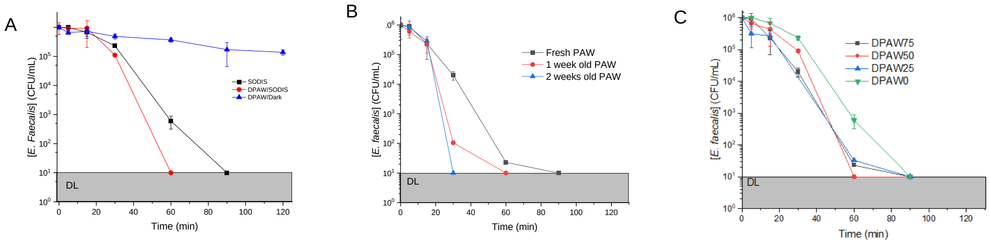

Figure 2. Information relative *E. faecalis* inactivation. In a reactor of 100 mL. A) Interaction of PAW and SODIS. B) Evolution of the efficiency of DPAW with time. C) Influence of the dose of DPAW.

Acknowledgements

This research has been supported by Comunidad Autónoma de Madrid through an industrial doctoral scholarship (IND2022/AMB-23691) to J.I. Quintana-Terriza.

Immobilisation of photocatalysts on spider silk-based membranes for continuous hydrogen production

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The environmental problems accompanying the use of fossil fuels demand new ways of energy production. H_2 is an important energy carrier and is seen as a fuel of the future. However, current methods to produce H_2 are energy consuming making them uncompetitive to conventional energy production. Photocatalysis is considered as an environmentally friendly way of producing fuels utilizing the almost unlimited supply of energy from the sun while using simple setups.[1]

Although particulate photocatalysis setups have been intensively studied in recent years, they exhibit major drawbacks, like difficult scalability. Due to the weight of water the production of thin panels is necessary, but the stirring of thin water layers is impractical making an equal distribution of the catalyst and an efficient transport of educts and products challenging. Furthermore, the recovery of the catalyst by centrifugation or filtration adds another problem leading to additional pollution.[2] The immobilisation of photocatalysts is therefore necessary to allow future large-scale applications for photocatalytic H_2 production.

Recombinant spider silk can be a possible candidate for the immobilisation of photocatalysts. While being a biomaterial with high toughness and tensile strength, it is also biodegradable making it an ideal material to avoid further pollution through (micro-)plastic waste. Genetic modification of the proteins implement binding motifs allows bonding between the fibres and the catalyst.[3]

In this work we will present meshes of recombinant spider silk proteins acting as support material for photocatalysts. Meshes were fabricated by electrospinning of the polycationic protein ntagCYSeADF4(κ16). Gold-decorated TiO2 nanoparticles were covalently bound to the fibres by a cysteine tag. We will show that catalyst particles are distributed homogeneously on the fibre confirming the successful bonding of the catalyst. Photocatalytic measurements show stable photocatalytic production of H_2 under 300W Xe lamp irradiation in water-methanol mixture. Finally, meshes were used in a flow reactor setup demonstrating the successful use as flow-through membranes supporting flow rates up to 1mL/min.

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The authors acknowledge financial support from the Bayerische Forschungsstiftung. Tim Schiller acknowledges support from the Elite Network of Bavaria. Many thanks to Dr. Hendrik Bargel for the support while taking the EDX data.

P-110

The chemistry point of view on porous silicon: oxide-free foils with seamless detachability through modulation of electrolyte composition

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Silicon is the most popular material used in electronics and optoelectronics due to its semiconducting properties, its natural abundance, and its competitive price. The development of thin and ultra-thin Si foils has marked the future of flexible optoelectronics, particularly in the field of photovoltaics.[1] In addition, ultra-thin Si foil fabrication enabled the possibility of substrate reuse after foil detachment, which results into a further advantage as 30% of the overall expenses for a silicon-based solar cell are attributed to the silicon material.[2] Porous silicon free-standing foils are typically prepared via electrochemical etching of tubular macropores patterned through photolithography and further sintered at high temperature. Alternatively, electrochemical etching of mesoporous silicon using a HF aqueous-based electrolyte allows fabrication of foils through a more affordable approach with a wider synthesis window in terms of pore size/type and porosity tunability.

Over the last few decades, the formation of a low porosity / high porosity 2-layer stack has been employed to produce such free-standing sintered porous silicon foils, but oxidation of the porous core and poor surface quality (for both the foil top/bottom surfaces and the parent substrate) has hindered its commercialization and its potential for parent substrate reuse.[3]

In this contribution we demonstrate the design and fabrication of a 4-layer structure with variable porosity using modulated electrolyte composition, that produced oxide-free, flexible free-standing foils through a "seamless" detachment from the substrate. Resulting sintered porous silicon foils are prepared over the range of 2 - 10 micrometers thick (Fig. 1a), exhibit low top roughness (RMS = 0.89 nm) that permits epitaxial growth (Fig. 1c) and reasonable roughness of the parent substrate for straight reconditioning (RMS = 8.71 nm) and reuse (Fig. 1d). The free-standing foils are highly flexible (Fig. 1e) and can be detached without cutting the parent substrate using commercial cello-tape even before sintering (Fig. 1e). The novelty of this work resides in the potential use of these foils as crystallographic templates in III/V photovoltaics, as well as its potential to design protocols to improve the design of detachable foils of other related materials such as Ge and GaAs.[4]

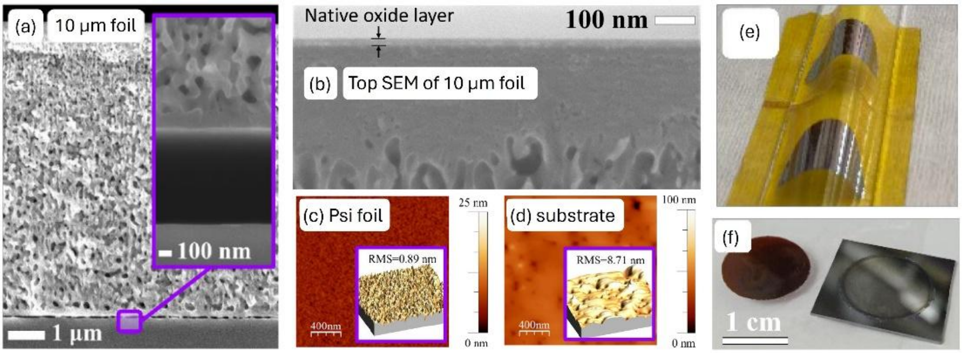

Fig. 1. (a) Cross-sectional SEM image of sintered porous silicon foils with "seamless" detachability. (b) Cross-sectional image of the surface of the porous silicon foils showing the pore-less surface with a protecting native oxide layer of approximately 10 nm. AFM images of (c) top of sintered porous silicon foil and (d) parent substrate surface after detachment. (e) Image showing the high flexibility of free-standing sintered porous silicon foils. (f) Image of a porous silicon foil that is readily detachable even before sintering just using cello-tape.

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The authors are indebted to Luis Cifuentes and Jesús Bautista for their unvaluable technical assistance. This work has been supported by grant PID2021-123530OB-I00 funded by MICIU/AEI/ 10.13039/501100011033 and FEDER, UE.

P-111

Exploring the disinfection of aquaculture matrices by Ga_2O_3/UV-C photocatalysis

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The global population increase and the consequent demand for food sources have driven the expansion of recirculating aquaculture systems (RAS) as a sustainable alternative for fish production [1]. This approach, however, is based on the intensive water recirculation and the need for a very water quality. Advanced Oxidation Processes (AOPs) have emerged as powerful alternatives for water disinfection, by the generation of highly reactive species which interact with waterborne pathogens [2]. Photocatalysis, as a heterogeneous AOP, emerges as a key solution for the integral water treatment that RASs require. This study investigates the application of Ga_2O_3/UV-C photocatalysis, and its intensification with peracetic acid (PAA), for the disinfection of *Enterococcus faecalis*, employed as a model microorganism due to its resistance and environmental relevance. Ga_2O_3 an emerging semiconductor material, offers a wide bandgap and chemical stability, making it a suitable candidate for UV-driven disinfection processes.

An UV-C batch system, equipped with a *PhotolabLED265-0.1er/cb* UV-C Lamp (Apria Systems, Ltd.), and operating in a 0.5-2.5 W/m^2 irradiance range is employed for the treatment of simulated aquaculture water, spiked with a 10^6 CFU/mL concentration of *E. faecalis* (ATCC 29212, Scharlab). Ga_2O_3 (Sigma-Aldrich) and peracetic acid ($C_2H_4O_3$, Panreac) were used as photocatalyst and oxidizing agent, respectively, without further purification.

The disinfection performance of Ga_2O_3/UV-C was first assessed under varying catalyst dosages. At an optimal concentration of 0.025 g/L Ga_2O_3, *E. faecalis* inactivation reached detection limit (DL = 10 CFU/mL) within 7.5 minutes of treatment, significantly outperforming UV-C alone. Increasing the Ga_2O_3 dosage beyond this point did not yield further improvements, likely due to light scattering or catalyst agglomeration. To enhance the process, PAA was introduced. The Ga_2O_3/UV-C/PAA system demonstrated synergistic effects. In particular, the combination of 0.025 g/L Ga_2O_3 and 0.05 mM PAA led to complete inactivation of *E. faecalis* in under 2.5 minutes, with all tested improving the Ga_2O_3/UV-C disinfection kinetics. The results highlight the key role of both PAA and photocatalysis presence in accelerating bacterial inactivation.

The Ga_2O_3/UV-C and Ga_2O_3/UV-C/PAA systems show strong potential for advanced water disinfection, offering rapid and efficient inactivation of *E.faecalis* under mild conditions. The PAA-intensified system achieved significative disinfection with minimal oxidant dosage and short reaction times. Future work will focus on comprehensive evaluation of the optimized system conditions, including reactive species identification via scavenging experiments, performance in real aquaculture water matrices, assessment of matrix effects, and monitoring of ionic composition and total organic carbon (TOC) in the effluent. These studies aim to validate the process for real-world application in aquaculture water treatment, as a first step to its scale-up.

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Photocatalytic Oxidation of Anisyl Alcohol using Carbon Nitride/Perovskite Composites

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Graphitic carbon nitride (GCN) is a metal-free photocatalyst that has been used for several applications (e.g. environmental remediation, H_2 production, CO_2 reduction, and organic synthesis) due to its high stability, low preparation costs and easy access to raw materials. In organic synthesis, GCN has proven to be an effective catalyst for the production of aldehydes under visible light and at mild operation conditions, while traditional methods often require harsh conditions, hazardous oxidizing agents and generate plenty of toxic by-products [1].

Although GCN exhibits a relatively wide band gap (~2.7 eV), it holds low charge carrier mobility and a limited number of surface redox-active sites, which hinder its photocatalytic performance. On the other hand, perovskite materials, such as $Cs_3Bi_2Br_9$ (CBB), have emerged as promising photocatalysts with interesting photoelectric properties [2]. Therefore, in this work, GCN/CBB composites were used to synthesise *p*-anisaldehyde (AAD) from the oxidation of anisyl alcohol (AA). GCN was produced by the thermal decomposition of dicyandiamide at 550 °C under airflow, and CBB was synthesised by mixing the $CsBr_3$ and $BiBr_3$ precursors with N,N-dimethylformamide in continuous stirring at 60 °C. The composites with different quantities of GCN (5 – 95 %) were obtained by adding GCN one hour after starting CBB synthesis.

The photocatalytic production of AAD was performed using 1 g L^{-1} of catalyst for 4 hours under visible LED irradiation. High-Performance Liquid Chromatography was used to identify and quantify the different aromatic species to assess the activity and stability of the catalysts.

A synergetic behaviour between both semiconductors was noticed with an exceptional increase of activity, even for catalysts with low amounts of CBB, when compared with GCN. The 70% GCN/CBB composite revealed the best balance between photocatalytic activity and stability, allowing a more sustainable production of AAD.

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P-113

Electrodeposited $BiVO_4$ Photoanodes for Solar-Driven Water Splitting and Organic Pollutant Degradation

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Bismuth vanadate ($BiVO_4$) is a promising photoanode material for photoelectrochemical (PEC) applications due to its favourable band gap (~ 2.4 eV) and visible-light absorption. However, poor charge carrier mobility and recombination losses often limit its performance [1,2]. In this work, we studied the synthesis of $BiVO_4$ transparent photoanodes via an optimized electrodeposition process, followed by a mild thermal treatment to control oxygen vacancies. Structural characterization by X-ray diffraction (XRD) confirms the formation of crystalline $BiVO_4$, with characteristic peaks observed after 1.5 h deposition at 2.6 V vs. Ag/AgCl (Fig. 1). The PEC performance of the electrodeposited $BiVO_4$ anodes is compared to spin-coated counterparts, highlighting the differences of electrodeposition in tuning film morphology and electronic properties [3].

Beyond fundamental characterization, we explore the versatility of these photoanodes in energy and environmental applications. In collaboration with Ricerca Sistemi Energetici (RSE), we investigate their use in PEC water splitting for H_2 production and in the oxidation of organic contaminants from industry wastewater.

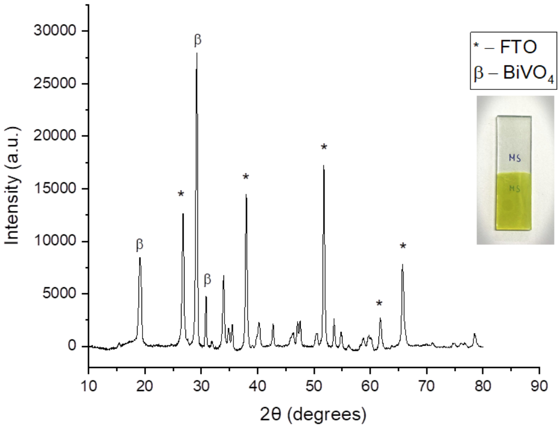

Fig. 1. X-ray diffraction (XRD) pattern of electrodeposited $BiVO_4$ film on FTO after 1.5 h deposition at 2.6 V vs. Ag/AgCl, whose photo is reported on the right side. The characteristic peaks of either $BiVO_4$ and FTO substrate are identified.

Ongoing characterization efforts include linear sweep voltammetry (LSV) to assess the photocurrent density under simulated solar light in the presence of hole scavengers or for direct water splitting and the charge transport properties of the material. Additionally, IPCE measurements will allow determining the spectral response of the electrodeposited $BiVO_4$. Additionally, we aim to optimize these photoanodes by incorporating dopant atoms (e.g. Mo) to enhance charge transport and co-catalysts to boost surface kinetics and charge separation efficiency.

Integrating heterojunctions with complementary metal oxides is also under consideration to further improve charge separation and performance in PEC applications [4]. These modifications will be explored for both solar-driven hydrogen production and organic pollutant degradation, highlighting the adaptability of the system for sustainable energy and environmental remediation.

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P-114

P-modified g-C_3N_4 for solar-driven photocatalytic H_2O_2 synthesis

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Hydrogen peroxide (H_2O_2) is attracting attention as mild, sustainable oxidant for environmental remediation and organic synthesis, as well as liquid fuel. However, the dominant production method via anthraquinone autoxi-dation process is highly energy-intensive and environmentally-costly, involving significant solvent use and release. Thus, there is strong interest in more sustainable, cost-effective synthesis [1]. In this context, photocatalytic H_2O_2 production stands out, as it uses water and oxygen as raw materials and solar light as energy input. Additionally, it enables simultaneous pollutant degradation, with the latter acting as proton donors (sacrificial agents).

Graphitic carbon nitride (g-C_3N_4) is a promising photocatalyst for energy and environmental applications, being visible light responsive, derived from Earth-abundant elements via facile synthesis, and possessing high stability and suitable electronic structure for O_2 reduction [2]. Yet, its performance is hindered by a low specific surface area (<10 $m^2\ g^{-1}$), poor conductivity, and rapid electron-hole recombination. which are responsible for low photocatalytic performances. To overcome these issues, various strategies have been explored, including exfoliation into nanosheets, defect and nanoarchitecture engineering, hard/soft templating, metal/non-metal doping, copolymerization, and coupling with carbon materials or other semiconductors.

This work investigates the efficiency of P-modified g-C_3N_4 photocatalysts for H_2O_2 synthesis from water and oxygen under solar light. The photocatalysts were obtained by thermal polymerisation of melamine at 550°C for 4 h (5°C/min heating rate) in the presence of sodium hypophosphite as phosphor source. The catalysts were denoted as xP-GCN, where x refers to the P wt.% content in the P-modified g-C_3N_4 photocatalysts.

This work proved the ability of P-modified g-C_3N_4 to synthesize H_2O_2 from water and oxygen under solar light. The effect of phosphorus content on the nanostructure and properties is discussed, and the activity is assessed in terms of H_2O_2 yield (mmol/g_{cat}), and apparent kinetic constants for H_2O_2 formation (mM·min^{-1}) and decomposition (min^{-1}). Controlled phosphor incorporation into the g-C_3N_4 structure significantly enhances photocatalytic performance, boosting the H_2O_2 formation rate by up to 4.5 times while maintaining a low decomposition rate. H_2O_2 synthesis under visible light (λ>420 nm) isolates the contribution of visible wavelengths to the overall solar activity. To understand better the reactional pathway, quenching experiments are conducted using $AgNO_3$ and p-benzoquinone as electron and $O_2^{\bullet -}$ scavengers, respectively, and pure water without the hole scavenger IPA.

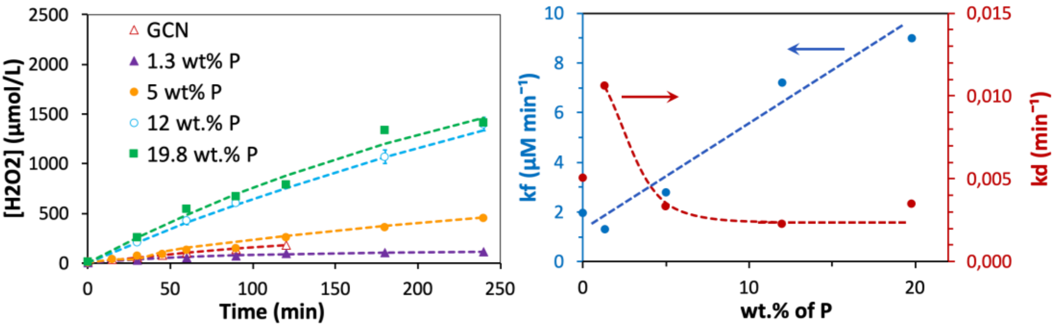

Fig. 1. Effect of Phosphorus content in g-C_3N_4 photocatalysts on (a) H_2O_2 production and (b) both apparent rate constants for H_2O_2 formation (k_f) and decomposition (k_d) under solar light. Conditions: [Cat] = 1 g/L ; 20°C ± 5°C; [Isopropyl alcohol, IPA] = 5 vol.% ; 10 mL/min air flow bubbling ; 500 W m^{-2} Xe lamp (Suntest XLS+ reaction chamber) ; [H_2O_2] determined by iodometry.

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This research was funded by the Interdisciplinary Institute HiFunMat, as part of the ITI 2021-2028 program of the University of Strasbourg, CNRS and Inserm, supported by IdEx Unistra (ANR-10-IDEX-0002) and SFRI (STRAT'US project, ANR-20-SFRI-0012). We acknowledge funding from the Initiative d'Excellence (IdEx) of the University of Strasbourg under LocalCat4Water project. This work was supported by the French National Research Agency in the frame of the project MULTICAT (ANR-23-CE07-0038).

P-115

Nanostructure ZnO Coatings as Antiviral Surfaces: Influence of Synthesis Methodology on Photocatalytic Efficiency

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Zinc oxide (ZnO) nanorods (NRs) thin films are promising materials for photocatalytic and antiviral applications due to their high surface area, tuneable morphology, and excellent optical properties.[1,2] In this study, ZnO NRs were synthesised via three distinct methods: sol-gel, hydrothermal, and aerosol-assisted chemical vapour deposition (AACVD). The influence of different seeding approaches−dip-coating and drop-casting−was systematically evaluated to optimise NR orientation, coverage, and crystallinity. Dip-coating led to c-axis texturing but exhibited uneven coverage, while drop-casting provided uniform layers with improved homogeneity, particularly when combined with hydrothermal synthesis. AACVD was explored as a catalyst-free alternative, achieving high crystallinity ZnO NRs with well-defined morphologies and enhanced preferential growth along the [001] direction.[3,4]

Structural and optical characterisations were conducted using SEM, GIXRD, and UV-Vis spectroscopy. AACVD-derived ZnO films displayed superior crystallinity and phase purity compared to solution-based approaches, with minimal defect-related absorption and a well-defined bandgap near 3.3 eV (Fig. 1). Photocatalytic antiviral tests using the MS2 bacteriophage under ambient white light (~1000 lux) demonstrated that AACVD-synthesised ZnO NRs achieved a 4-log (99.99%) reduction in infectivity within 2 h, outperforming solution-based methods, which achieved only a 2-log reduction under identical conditions (**Fig. 1**). The enhanced performance of AACVD films is attributed to their higher crystallinity, reduced carbon contamination, and improved charge carrier dynamics.

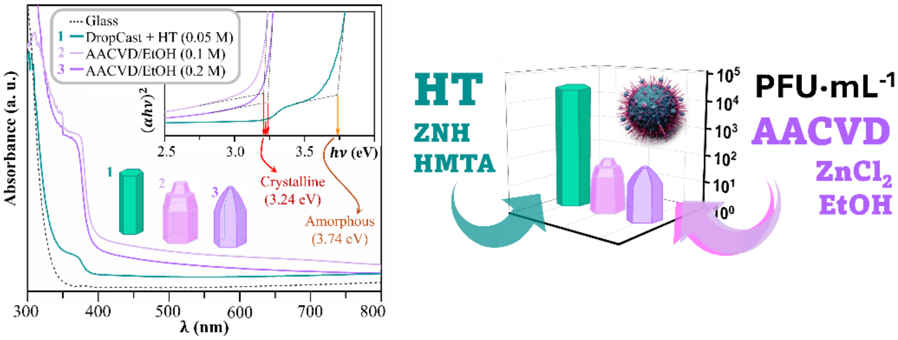

Fig. 1. Absorbance in the visible range and tauc plot (inset) of selected ZnO NSs film coatings with rod-like nanostructures. Dotted black lines represents the absorbance of the glass substrate, the red arrows indicate the bandgap of crystalline ZnO, and the orange arrow indicates the bandgap of amorphous ZnO. Viable counts of bacteriophage MS2 after exposure to standard laboratory white light (1000 lux) of ZnO film coatings produced by wet chemistry methods (HT, green rod) and AACVD processes (purple rods).

These findings highlight the critical role of fabrication techniques in determining the photocatalytic and antiviral efficiency of ZnO coatings. AACVD emerges as a highly scalable and efficient approach for producing high-performance ZnO-based photocatalysts, offering a promising route toward the development of next-generation antimicrobial surfaces for real-world applications.

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Thin film design: how does the architecture of rutile and anatase impact the photocatalytic properties?

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In previous studies, it was found that rutile is more beneficial for reduction targets, whereas anatase is optimal for oxidation targets [1]. Because this study was performed on powder samples it was impossible to eliminate the influence of the surface area. Herein, similar investigations were performed using thin films of titania.

In this work, the thin layers containing anatase and rutile compositions were designed to investigate how the architecture influences the reduction/oxidation in photocatalytic properties. The influence of synthesis conditions on the thickness, morphology, and crystalline form of TiO_2 nanolayers on a silicon substrate was investigated. TiO_2 coatings were synthesized using the sol-gel method and dip-coating followed by calcination at temperatures ranging from 500 °C to 1000 °C. The correlation of the crystal structure with the thickness of the coating was possible by controlling the number of immersions in the sol and the calcination time. It was found, that limiting the coating thickness to the nanometer scale changes the crystallization conditions and inhibits the growth of crystallites, preventing the phase transition from anatase to rutile. This results in a change in the thermodynamic stability of TiO_2 polymorphs, related to the surface energy and grain size [2]. The phase transition depends not only on the type of substrate, as previously proposed by Miszczak and Pietrzyk[3], but also on the thickness of the thin film. The design of thin films enables the control of the oxidation/reduction properties of titania coatings.

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P-117

What determines the photocatalytic activity of g-C_3N_4-Co_xO_y in methanol photoreforming?

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The answer to current challenges in the search for sustainable energy sources is solar fuels, which can be provided by photocatalysis. Methanol photoreforming has emerged as a promising technology, and in comparison to water-splitting, it has significantly lower reaction energy, making it more available [1]. In this case, graphitic carbon nitride reveals interesting, as it is very stable, cheap, and enables harvesting visible light. However, because of its limitations, e.g. fast recombination of electron-hole pair, it did not meet the expectations of efficient technology. To overcome disadvantages, one of the promising options is to design nanocomposites, creating efficient heterojunctions, which allow to reach high hydrogen productivity [2].

A simple synthesis of g-C_3N_4-Co_xO_y was developed, in which primary CoO microcrystals turn into nanoparticles while the thermal polycondensation of the host matrix occurs. The study of the process revealed that depending on the amount of initial CoO, two concurrent processes occur: in-situ growth of g-C_3N_4 and oxidation of CoO to Co_3O_4 with accompanying combustion of g-C_3N_4. These processes were analyzed in detail using *inter alia* SEM-EDS, BET, FTIR, XRD, and XAS. The photocatalytic activity of synthesized composites was tested in methanol photoreforming, revealing that the +3 oxidation state of Co plays a key role in boosting hydrogen evolution. It was found that the methanol photoreforming follows mainly the direct oxidation pathway.

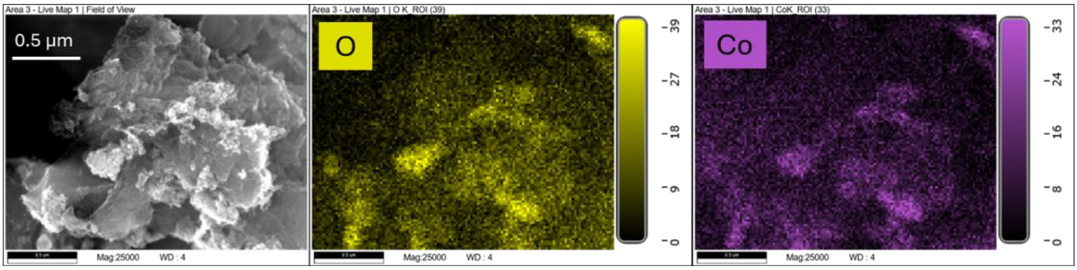

Fig. 1. SEM image of g-C_3N_4-Co_xO_y nanocomposite (left) and corresponding elemental map of oxygen (middle) and cobalt (right).

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P-118

Photocatalytic films – from glass to polymers

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While the development of photocatalytic materials has done large steps in terms of efficiency and working range from their inception in the 1970s, the application of these materials hasn't followed the trend [1].

Herein, we explore several attempts to immobilize various photocatalysts (mostly TiO_2, but also ZnO, CuO and g-CN) onto various substrates. These range from the most used glass all the way to the more structurally adaptive common polymers. Immobilization of nanoparticles using a reasonably priced and industrially friendly processes is desired especially if the technology is to achieve the long-hoped widespread use across multiple industries. While adhesion to the substrate is of utmost importance, in case of a multilayered system the cohesion forces also become important. A robust adhesion substantially relies on interfacial wetting. However, strong adhesives usually improve cohesion but compromise interfacial properties, i.e., highly viscous polymeric adhesives make their penetration or wetting to the substrate kinetically slow under application conditions. Additionally, direct contact between the adhesive and adherend substrate is desired and it is achieved by the interaction between the substrate surface groups to and the adhesive functional groups. A clear example is shown in Fig 1 where two PET foils exhibit different surface chemistry and show dramatically different adhesion properties of an exemplary TiO_2–SiO_2 sol-suspension.

In this regard, fundamental aspects regarding the choice of substrate and, more importantly, the design of photocatalytic sol-suspension will be discussed. The applicative side of the research will be focused on self-cleaning surfaces [2], air remediation devices [3] and surfaces for water disinfection reactors [4], [5].

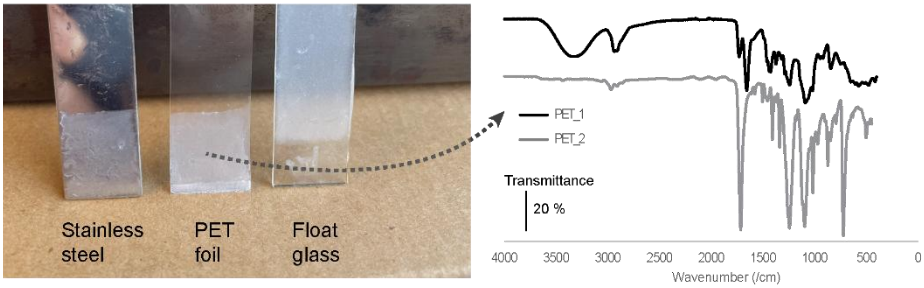

Fig. 1. A TiO_2–SiO_2 sol suspension immobilized via dip-coating onto three different substrates (left) and ATR-FTIR spectra of the two PET foils tested for coating.

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Acknowledgements

This work was financially supported by the Slovenian Research and Innovation Agency through the projects No. J1-2472, No. J2-4444 and No. J2-4441, as well as core programs No. P1-0134 and No. P1-0418. We acknowledge NETPORE COST Action CA20126 for their support.

Effect of vanadium pentoxide on the material characteristics and photocatalytic activity of strontium titanates

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A composite photocatalyst was prepared using vanadium pentoxide (V_2O_5) and strontium titanate ($SrTiO_3$) to investigate the composition-dependence of photocatalytic activity. The samples were characterized by X-ray diffractometry, diffuse reflectance spectroscopy, photoluminescence spectroscopy, Raman spectroscopy, X-ray fluorescence spectroscopy and linear sweep voltammetry. The photocatalytic activity of the samples was evaluated by phenol degradation under UV light irradiation. A commercial $SrTiO_3$ without V_2O_5 was used as a reference. The composites contained V_2O_5 in the following concentrations: 0, 1, 2, 4, 6, 8 and 10 wt%. The results showed that V_2O_5 had a positive effect on the photocatalytic activity of $SrTiO_3$, therefore it is an excellent cocatalyst under the applied conditions.

Acknowledgements

Áron Ágoston acknowledges the Doctoral Student Scholarship Program of the Co-operative Doctoral Program (EKÖP-KDP-24-SZTE-6) of the Ministry of Innovation and Technology financed from the National Research, Development and Innovation Fund. The authors are grateful for the financial support of the 2021-1.2.6-TÉT-IPARI-MA-2022-00009 project. Project no. TKP2021-NVA-19 has been implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-NVA funding scheme.

P-120

Characterization of lead-free Cs_2SnI_6 perovskite and its ecotoxic effects on isopods

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$CsPbX_3$ semiconductor perovskites are considered as a promising material in the research and the development of new types of solar cells. However, its lead-related toxicity raises several concerns, such as oxidative stress, carcinogenicity, developmental toxicity. One of the possibilities to reduce their toxicity is by replacing Pb with other metallic elements.

In the present work, Cs_2SnI_6 lead-free perovskite was synthesized by solvothermal method at different temperatures (120 °C, 150 °C and 180 °C) with the aim to investigate the environmental impact of the differently synthesized nanoparticles. The material structure, morphological and optical properties of the samples were characterized by XRD, SEM and DRS material analysis methods.

The samples were stable in air for the duration of the test, but in contact with water, a rapid decomposition followed, and the material lost its crystal structure. This process was partially reversible, as the material recrystallised from its medium after drying. Further dissolution-crystallization sequences also resulted in a decrease in crystallinity, due to the loss of iodine content, and the material contained increasing amount of CsI.

An important criterion for environmentally stable materials is that they retain their original form in different media. For unstable materials, the release of various chemical species may be responsible for toxicity, therefore it is of particular importance to investigate the effects of these on the environment.

In the toxicological experiment, habitats with increasing concentrations of a selected sample were established to monitor the population changes of the isopods (*Porcellio laevis*) and the stability of the released material in the environment. The protocol was to follow the life cycle of 15 individuals (10 adults and 5 developing individuals) for one month. The soil was amended with 0, 0.1, 0.5 and 1.5 wt% perovskite and the living conditions (soil thickness, water, food source, calcium source) were adapted to the species. No mortality occurred in the control experiment (0 wt%). Significant declines in numbers were observed in the 0.1 and 0.5 wt% experiments, and 100% mortality in two weeks in the 1.5 wt% experiment.

Acknowledgements
The authors are grateful for the financial support of the 2021-1.2.6-TÉT-IPARI-MA-2022-00009 project.

P-121

DACs@TiO_{2-x} for photothermalcatalysis of polyethylene

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The high production and short lifespan of plastics have led to a surge in plastic waste (PW), with approximately 72% of PW being incinerated or landfilled, posing a continuous threat to biodiversity and ecosystem balance. In China, over 90% of PW is composed of highly chemically inert polyolefins (C-C bond energy ≈ 348 kJ/mol, C-H bond energy ≈ 414 kJ/mol), which needs to be effectively degraded under harsh conditions such as high temperature (>500 ^oC), high pressure (>20 atm), and strong acid or alkali. Photothermalcatalysis, as a technology that synergistically utilizes heat and light energy and combines the advantages of photocatalysis and pyrolysis, has become a new paradigm. TiO_{2-x} nanospheres loaded with dual atoms (DACs) with different RuCu ratios were designed and constructed for photothermalcatalysis of polyethylene. CO_2 is used as a weak oxidant to co-degrade with polyethylene into synthesis gas. When the ratio of Ru to Cu is 2.5:10, the degradation rate is the highest, and the H_2/CO_2 ratio is 2.75.

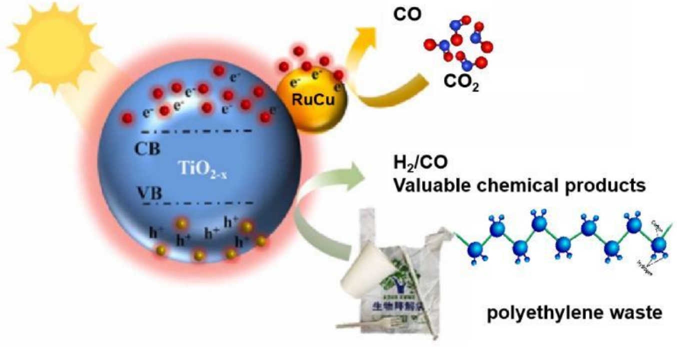

Fig. 1. Reaction mechanism of photothermalcatalysis on Ru-Cu DACs@TiO_{2-x}.

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Fabrication and Characterization of Dual-Phase Tungsten Oxide Thin Films Made by Direct Patterning

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Tungsten oxide is a non-toxic inorganic semiconductor with excellent photocatalytic activity under ultraviolet and visible light irradiation. This is due to the lower bandgap of under 2.8 eV, in comparison with more widely used titanium oxide [1]. Such properties establish tungsten oxide as an interesting candidate for environmental applications, like photocatalysis, photo-electrodes, dye-sensitized solar energy devices and solar cells [2]. However, metal oxides composites and thin layers are usually prepared using complicating and often environmentally unfriendly methods.

Semiconductor photocatalysts are generally synthesized in two different ways: disintegration of crude material by mechanical processing (top–down), or assembly of atoms and molecules into desired nanoparticles (bottom–up). Each of these methods have their own advantages and disadvantages. Combining these two fundamentally different methods into one could bring out advantages and reduce disadvantages of each, while creating new properties. Such dual-phase material would be consisting of top–down prepared nanoparticles ("bricks") and bottom–up prepared amorphous matrix ("mortar") [3].

The aim of this work was to prepare thin films of tungsten oxide using different deposition methods from aqueous WO_3 composite to accommodate a greater need for environmentally friendly materials. For this purpose, combination of wet ball-milled WO_3 nanoparticles and solution of amorphous precursor ammonium metatungstate (AMT) were deposited on fluorine-doped tin oxide glass substrate. The WO_3 nanoparticles with multimodal distribution act as building blocks, while the amorphous binder fills space between them and connecting nanoparticles to each other, as well to the FTO glass substrate. Templating agents were added into the composition to obtain a porous structure by removing them during calcination. Final compositions were deposited using various coating methods and annealed at high temperatures to obtain thin layers.

The effect of differently prepared compositions on the physicochemical properties of deposited layers was studied, as well as the effect of different coating processes on layer thickness, structure and photocatalytic properties. The layer surface was analysed using scanning electron microscope and the layer thickness using mechanical profilometer. The photoelectrochemical properties were studied using linear sweep voltammetry and chronoamperometry using sources with different wavelengths.

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Acknowledgements

This work was supported by Czech Technology Agency through project TH03030197.

P-123

Photocatalytic Approaches for Plastic Degradation in Water

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Plastic pollution and its harmful environmental effects have been recognized for decades, but they have recently become a global concern. According to Plastics Europe [1], 413.8 million tonnes (Mt) of plastic were produced worldwide in 2023 — 43 Mt more than in 2018. However, only about 10% (< 40 Mt) was effectively recycled in Europe, primarily through mechanical recycling, while more than 20% evaded waste management systems, ultimately polluting the environment. Once released, plastics undergo fragmentation and degradation *via* abiotic and/or biotic processes, leading to the formation of smaller and more reactive particles. Fragments < 5 mm (along their largest dimension) are classified as microplastics, which can further degrade into nanoplastics (< 1000 nm) and oligomers (<10,000 Da) [2]. Although wastewater treatment plants remove approximately 90% of the microplastics, they remain a major source of plastic contamination in freshwater and marine ecosystems [3]. To address this issue, numerous strategies have been proposed to degrade or transform plastics in water, including photocatalysis.

This study aims to develop efficient photocatalytic systems for the degradation of nanoplastics and submicrometric oligomer particles in water. Photocatalysts based on commercial TiO_2 (Aeroxide® P25) and g-C_3N_4, combined with Metal-Organic Frameworks (MOFs), were explored. TiO_2 P25 was chosen as a benchmark due to its well-documented photocatalytic activity, stability, and optimal anatase-to-rutile ratio. Meanwhile, g-C_3N_4 was selected as a promising alternative, since it can be activated by visible light, is synthesized from Earth-abundant elements through simple methods, and exhibits high physico-chemical stability along with a unique electronic band structure [4]. Additionally, MOF-based photocatalysts offer several advantages, including high porosity, numerous charge transfer pathways, abundant active sites, and efficient adsorption-desorption channels [5].

The crystalline structure and optical properties of the photocatalysts were characterized by X-ray diffraction (XRD) and UV–vis diffuse reflectance spectroscopy (DRS), respectively. Photoelectrochemical properties were analyzed using transient photocurrent (TPC) measurements in a three-electrode cell configuration (working volume: 50 mL) with 0.1 M Na_2SO_4 as the electrolyte. A graphite felt (4 cm^2) coated with the catalyst served as the working electrode, while a graphite rod and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Measurements were conducted using a Metrohm Autolab PGSTAT101 potentiostat under LED illumination at 365 nm (Mightex LED BLS 13000–1), 415 nm (Thorlabs M415LP1), and 450 nm (Thorlabs M450LP2).

The photocatalytic performance of the different catalytic systems was evaluated for the degradation of soluble polymers, specifically low-molecular-weight polyethylene glycol (PEG) and polyvinyl alcohol (PVA), in a beaker-type glass slurry reactor. Reactions were carried out under optimized LED irradiation conditions, determined from the DRS and TPC analyses. Polymer degradation was monitored by total organic carbon (TOC) and chemical oxygen demand (COD) measurements.

The results provided insights into the key factors influencing polymer breakdown under photocatalytic conditions, including catalyst properties, charge transfer dynamics, and irradiation wavelength. This study contributes to the development of advanced photocatalysts for mitigating plastic pollution in aquatic environments.

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Acknowledgements

LV thanks the Ministry of Science, Innovation and Universities for her Beatriz Galindo contract (reference BG23-00007).

P-124

A kinetics of singlet oxygen generation on printed photoactive layer

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Surfaces with antiviral and also antibacterial function have become modern and in demand. Surface sterilization is a one-time action, usually followed by the colonization of surfaces by viruses and bacteria when people touch them. All touch screens have become hazardous and have started to be fitted with special films that are supposed to have an antiviral and antibacterial function.

We present a self-adhesive printed film with an antiviral and antibacterial function, acting thanks to organic biocides in extremely low concentration, but thanks to the synergistic effect of photogenerated singlet oxygen. The thin printed layer of 1 to 3 microns thickness on the self-adhesive film contains a two-component polymer system with chemically bonded zinc phthalocyanine. These layers were printed on polyethylen terephtalate, polyvinylchloride and polyethylene foil.

Prior to consumer testing, the printed photocative layer had to undergo numerous tests to verify all microbiological and mechanical properties. The vast majority of the tests are extremely time and labour intensive. These include antimicrobial tests (ISO 27447 and ISO 22196), antiviral tests (ISO 21702), mechanical tests according to ISO 15184 and ISO 2409:2007.

However, the quickest test to indicate the photochemical activity of the photoactive layer is the test for the rate of singlet oxygen formation on the irradiated surface. For this purpose, an apparatus was constructed with a measuring cuvette with a sample of a film with a photoactive layer on the wall of the cuvette irradiated by two LEDs with a wavelength of 650 nm. Perpendicular to the direction of irradiation, the absorbance of the reaction solution was measured using a fibre spectrophotometer. The rate of change in absorbance of the reagent is directly proportional to the rate of singlet oxygen generation, and thus a measure of the ability of the photoactive layer to destroy bacteria and viruses on its irradiated surface. At the same time, the kinetics of singlet oxygen generation was studied using several organic reactants and dyes (1,3-diphenylisobenzofuran, resazurin and others).

Acknowledgements

This work has received financial support from the Technology Agency of the Czech Republic.

UV-B disposable dosimeter

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Treatment of various dermatoses with UVB radiation is very successful, but not without risk. Exposure to this radiation for too long causes problems similar to sunburn from normal sun exposure. It is therefore up to the physician to correctly determine the duration and therefore the dose of radiation for each patient based on their phototype, and the radiation dose must also be adjusted according to the individual patient's response.

The moment erythema appears on the skin, it is certain that the radiation dose was too high. This should never happen. Measuring radiation doses between zero and the appearance of erythema directly during irradiation using instrumentation is not always possible. A simple radiation dose indicator is suitable for this purpose. In the case of the use of a disposable UVB dosimeter, the main advantage is the ease of use under any conditions. The main requirements for a dosimeter are that it is easy and cheap to manufacture and use, that it gives a clear indication of the dose achieved, that this indication is irreversible and that it does not depend on the intensity of the source but only on the dose.

Common phototypes in our environment include phototype I and II. These people have very fair skin and are sensitive to sunburn, even their recommended therapeutic dose of radiation will be low. In general, 500 and 1,000 $mJ \cdot cm^{-2}$ are recommended for them, respectively.

Disposable UVB dose indicators – UV-B dosimeters – were prepared from a polymer matrix, photosensitive substance, acid-base indicator, auxiliary and calibration compounds. They were tested using a Philips PL-S 9W/01 narrow-band mercury lamp with maximum emission at 313 nm. The mixture was screen-printed on a RokuPrint 05 semi-automatic machine using a 140-31Y screen with a theoretical ink transfer volume of 12.5 $cm^3 \cdot m^{-2}$, corresponding to a wet film height in µm, that is 12.5 µm.

Tests were carried out for the insensitivity of the dosimeter to radiation with a wavelength greater than 340 nm and simultaneously for the reciprocity of radiation doses, i.e. that the colour change of the dosimeter depends only on the abstracted dose of UVB radiation and not on the intensity of this radiation.

Our disposable UVB dosimeter was prepared by printing in two sensitivity variants, with a colour change after absorbing a dose of 500 and 1000 $mJ \cdot cm^{-2}$.

Acknowledgements

This work has received financial support from the Technology Agency of the Czech Republic

P-126

Inverse Opal Titania Modified with Gold for Visible-light Photocatalytic Activity

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Photonic crystals, particularly inverse opals, have been applied in optical fields for decades [1]. More recently, many studies have focused on their application in photocatalysis due to high photocatalytic activity, achieved by a unique feature of slow photon effect [2,3]. Additionally, visible-light photoactivity is recognized as an important path for the development of photocatalysis. Therefore, this study aims to obtain visible-light activity based on titanium(IV) oxide (TiO_2, titania) inverse opal (IOT). In this regard, noble metals, such as gold nanoparticles (Au NPs), have been incorporated in IOT structure to utilize visible-light activity arising from the localized surface plasmon resonance (LSPR) effect [4].

The procedure of this study includes the fabrication of Au-IOT films, their characterization, and the evaluation of resultant photocatalytic activity. The initial step involves fixing IOT on a substrate - a basic platform for further processes. Although, the synthesis of IOT involves usually at least three steps, i.e., (i) opal template formation, (ii) inverse opal formation, and (iii) crystallization, here two first steps have been combined by a co-assembly method. Titania infiltration proceeds simultaneously with the formation of polystyrene (PS) opal. Accordingly, fast formation of IOT with high quality and without extra cracks (caused by capillary force during infiltration) has been succeeded. Moreover, the second step, i.e., the removal of PS opal template combined with TiO2 crystallization, eliminates additional heat treatment. Furthermore, to obtain gold-modified IOT, a novel three-phase co-assembly method has been developed to combine PS opal template, TiO_2 infiltration, and Au NPs' deposition.

The synthesized Au/IOT film exhibits a well-ordered face-centred-cubic structure as shown in the SEM image (Fig. 1a). The photonic bandgap (PBG) of IOT was illustrated in the transmittance spectra in Fig. 1b, which also display the LSPR absorption peak measured from absorbance of Au NPs suspension. By utilizing angle-dependent property of PBG, the red-edge of PBG can be tuned to overlap with the LSPR peak.

Photocatalytic performance has been evaluated by measuring hydroxyl radicals' generation under full spectrum irradiation while the incident angle was adjusted as the insets shown in Fig. 1c. Interestingly, radicals' generation rate is highly related to the incident angle. The optimal incident angle is 20°, which can be attributed to the matching of the PBG red-edge and LSPR absorption peak (Fig. 1c). Samples measured at 0° and 10° (IOT-0° and IOT-10°) show lower activity due to the intensive reflectance of PBG that hinders the photoabsorption. In contrast, PBG of IOT-30° and IOT-40° are out of the LSPR absorption region, leading to higher hydroxyl radicals' generation rate.

Concluding, synergistic coupling of slow photon effect and LSPR effect results in enhanced visible-light activity. Briefly, electrons generated through LSPR excitation transfer from Au NPs to conduction band of TiO_2. Meanwhile, the slow photon effect improve the photoabsorption in the range of LSPR and amplify the visible-light activity.

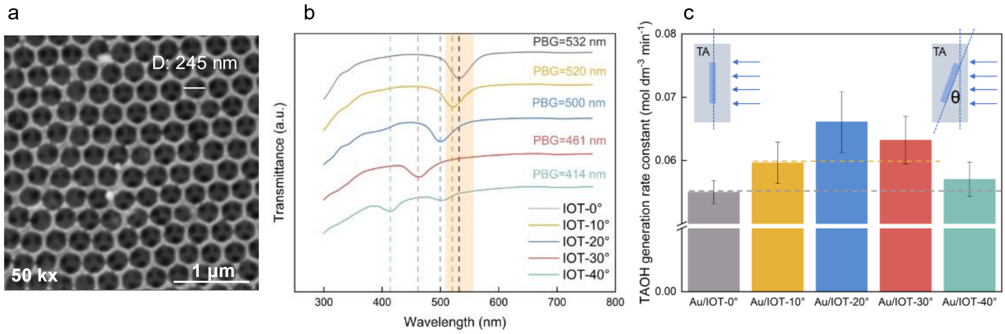

Fig. 1. a) SEM image of Au/IOT, b) transmittance spectra of IOT and LSPR absorption region from Au NPs suspension, c) angle-dependent photocatalytic performance of Au/IOT through hydroxyl radicals' generation, the insets are angle adjustment setup.

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This research has been co-founded by the Polish National Agency for Academic Exchange within Polish Return Program (BPN/PPO/2021/1/00037) and the National Science Centre within OPUS project (2023/51/B/ST4/01935).

Photocatalytic pre-treatment of lignin as a strategy to boost biogas production

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Lignin, a complex aromatic polymer and a major component of lignocellulosic biomass, poses a significant challenge for anaerobic digestion due to its high resistance to biological degradation [1]. To improve its biodegradability and enhance methane yields, effective pre-treatment strategies are required. Among them, TiO_2-based photocatalysis offers a promising method for low-input approach for breaking down recalcitrant organic compounds under mild conditions [2].

This study investigates the use of photocatalytic pre-treatment to decompose lignin and improve its conversion efficiency during anaerobic digestion. The photocatalytic decomposition of lignin was performed in a batch quartz-glass photoreactor (680 ml, Fig. 1a), using a suspension of 400 ml demineralized water, 0.2 g of TiO_2-P25, and 0.5 g of coffee grounds. The suspension was stirred (350 rpm) and purged with helium (1250–1275 kPa) for 30 minutes. After sealing, a gas sample was collected prior to UV-C irradiation (λmax = 254 nm) by the pen-ray lamp, which was vertically positioned inside a quartz tube in the reactor center. Gas samples after 48 irradiation hours were analyzed using GC (Shimadzu Tracera GC 2010Plus) with a barrier discharge ionization detector (BID), confirming the formation of H_2, CH_4, and CO. Control experiments without the photocatalyst (photolysis) were also conducted. After reaction, solid residues were separated, dried (8 h at 40 °C), and analyzed for residual lignin content to evaluate degradation efficiency. Subsequently, the solids were tested for biochemical methane potential (BMP) to assess biogas yield enhancement after photocatalytic pre-treatment prior to anaerobic digestion. The BMP test (Fig. 1b) was conducted under anaerobic conditions at a temperature of 40°C for a duration of 35 days. The results demonstrated enhanced methane yields, confirming the potential of photocatalytic pre-treatment as an effective strategy for valorizing lignin-rich biomass in biogas production.

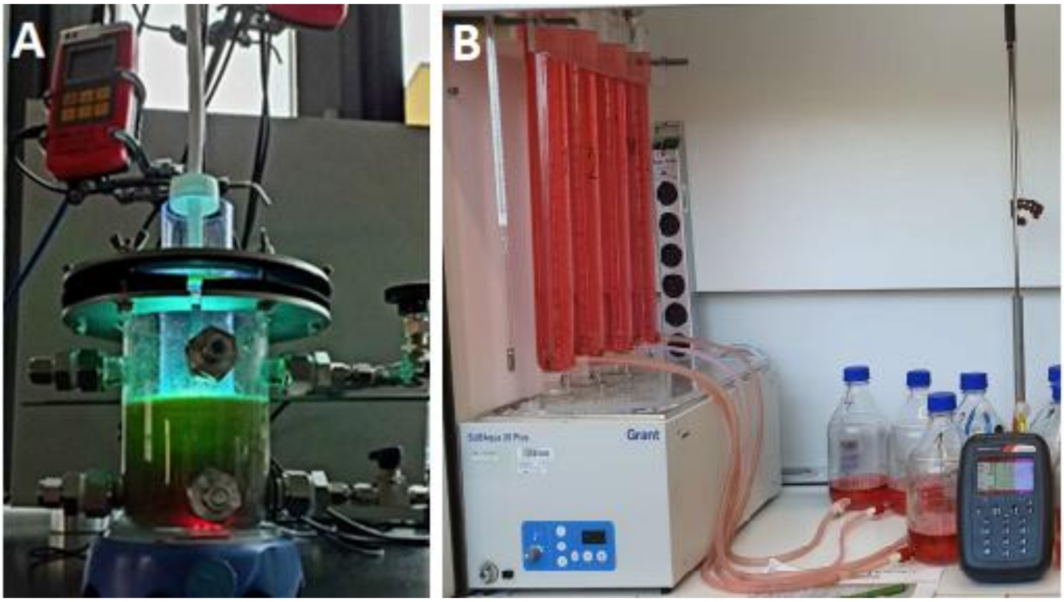

Fig. 1. (a) Batch quartz-glass photoreactor, (b) Experimental setup for the BMP test.

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Photoactivity of WO_3 films by liquid phase deposition

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Charge recombination is the main factor limiting the photoelectrochemical and photocatalytic efficiency of electrodes, including tungsten trioxide-based photoanodes. This problem can be mitigated by nanostructuring of the active material, which leads to a decrease in charge diffusion path and enhances minority charge injection from the semiconductor to the electrolyte. An interesting route to further improve the separation of photo-induced charges involves the formation of a two-phase layer with a gradient variable phase composition. Such a gradient is expected to provide a multitude of local heterojunctions along with a continuous change in reduction/oxidation behaviour across the active layer, leading to enhanced charge separation.

The liquid phase deposition (LPD) is a promising method for obtaining metal oxide thin films [1]. It is based on the slow hydrolysis of a metal-fluorine complex, and the rate of the reaction is controlled by a fluoride ion scavenger like H_3BO_3 or Al. The reaction occurs at ambient conditions and therefore can be competitive with other chemical deposition processes, *e.g.*, sol-gel or hydrothermal methods. Moreover, LPD was shown to be suitable for fabricating gradient layers [2].

In this study, the photoactive layers of WO_3 were deposited by the LPD method on bare and anatase-coated FTO glass substrates, and then calcined in air. Independent of substrate, the obtained films crystallized with monoclinic γ-WO3 structure and were composed of thin plates (thickness < 100 nm) forming dessert-rose-like aggregates. On the other hand, the quality of the layer (surface coverage, adhesion to the substrate, presence of agglomerates) and the morphology of aggregates depended not only on the pre-treatment of the substrate but also on the concentration of the tungsten-fluoride complex in the reaction solution. The optical band gaps derived from diffuse reflectance spectra were below 2.85 eV. The optimized films revealed maximum incident photon to current efficiency of 10-20% at potentials above 1 V *vs*. RHE. Photocurrent doubling effect was observed in the presence of methanol, indicating that hole injection kinetics at the semiconductor-electrolyte interface could be improved. Dessert-rose morphology seems to weaken adhesion of the film to the substrate, which consequently limits the photoelectrochemical efficiency of the electrodes. On the other hand, such a morphology can be beneficial for photocatalytic reactions, which was verified through the photocatalytic hydroxylation of terephthalic acid. The performed experiments are the first step towards the fabrication of gradient layers.

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This work has been supported by the National Science Centre (NCN; Poland) within the OPUS23 project (2022/45/B/ST5/04087).

On Distinguishing Energy and Electron Transfer in Photocatalytic Processes of Heteroatom-Doped Carbon Dots

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This study investigates the fundamental mechanisms governing photocatalytic activity in carbon dots (CDs) by examining the impact of surface chemistry and strategic heteroatom incorporation. Through systematic analysis of both non-metal (N, S) and metal (Cu, Zn, Ag, Au) doped CDs, we elucidate the distinct roles of energy and electron transfer pathways in reactive oxygen species generation. All synthesized CDs underwent rigorous purification before comprehensive characterization.[1] Photocatalytic singlet oxygen production was quantified via endoperoxide formation,[2] while hydroxyl radical generation was assessed through peroxide-assisted hydroxylation of terephthalic acid.[3] Our findings reveal a mechanistic differentiation where certain dopants selectively enhance either energy or electron transfer processes. Fluorescence lifetime analysis demonstrated that extended photon emission generally correlates with increased singlet oxygen production, with variations dependent on the specific heteroatom incorporation. Notably, our results revealed distinct mechanistic patterns across dopant types: while all metal-doped samples facilitated energy transfer processes, only copper-doped CDs exhibited significant electron transfer capability. In contrast, the non-metal doped series demonstrated more complex behavior without a clear trend in mechanism preference. Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) analyses confirmed that partial crystallinity and specific configurations of surface functional groups including S=O, –OH, and –COOH, serve as critical determinants of the predominant photocatalytic pathway. This investigation advances our understanding of the key factors that regulate photocatalytic mechanisms, either energy or electron transfer processes, in carbon dot systems.

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Enhanced photodegradation of tetracycline using graphene-like biochar-modified iodine/nitrogen co-doped TiO_2 (g-B/I-TiO_2)

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The increasing presence of emerging contaminants such as tetracycline (TC) in aquatic environments poses significant ecological risks. To address this issue, the study explores the transformation of agricultural waste (water caltrop shells) into high-performance graphene-like biochar and iodine and nitrogen-doped composite photocatalysts. This approach aligns with circular economy principles and provides a sustainable method for environmental remediation. Graphene-like biochar was prepared via hydrothermal treatment and pyrolysis at 500–900 ℃ with varying residence times. The composite photocatalysts (B/I-TiO_2) were synthesized by incorporating iodine (0.5 wt%) and nitrogen using sol-gel and hydrothermal techniques. Structural, surface, and functional analyses were conducted using TEM, BET, and surface charge measurement. Photocatalytic activity was assessed by TC degradation under visible light (410 nm) at different pH conditions. Graphene-like biochar exhibited a significantly enhanced surface area of 1529.1 m^2/g at 700 ℃ and 6 hours of hydrothermal treatment, demonstrating improved graphitization and reduced defects ($I_D/I_G = 0.80$). Photocatalytic tests revealed that the composite photocatalyst achieved a 99% TC degradation efficiency within 120 minutes under neutral conditions (pH 7). The iodine and nitrogen dopants effectively extended the electron-hole recombination time, enhancing the photocatalytic activity. The combination of biochar (5 wt%) and iodine (0.5 wt%) yielded optimal degradation results, supporting the potential of this system for sustainable water treatment.

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$C_3N_3S_3$ (TMT) with cobalt as a new material for photo- and photoelectrochemical water splitting

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$C_3N_3S_3$ (TMT) is organic semiconductor with ambipolar properties. This polymer has obtained more attention due to the visible light absorption by disulfide units (-S-S-) and delocalization of π bonds in triazine ring. It can be used in the reactions of oxygen reduction and photocatalytic hydrogen generation. However, the efficiencies of these reactions are still not satisfactory. [1] One of the possibilities of improvement may be a doping it with metals, such as Ni, Cu, or Cd, which introduced into the polymer act as active sites, prevent rapid recombination and increase conductivity.

In this work we try to make metal-polymer network of triazine trithiolate containing Co. Due to the value of the standard potential (Co^{3+}/Co^{2+}, 1.82 V), cobalt in the obtained photocatalyst may help in the reaction of water oxidation to oxygen. According to UV–vis-NIR absorption spectrum, CNS-Co can be employed as a board spectrum-driven photocatalyst for water splitting into hydrogen.

During the studies three different samples were synthesized: $Co_3(TMT)_2{\cdot}nH_2O$, $Co(HTMT){\cdot}nH_2O$, $Co(H_2TMT)_2{\cdot}nH_2O$ [2]. All samples were characterized by microscopic (SEM) and spectroscopic methods (UV-Vis, IR, and XPS). The difference between synthesized samples are shown on normalized FTIR spectra (Fig. 1).

The obtained samples were used for photocatalytic water splitting and electrochemical water oxidation with the use of $BiVO_4/M_x(TMT)_y$ composite.

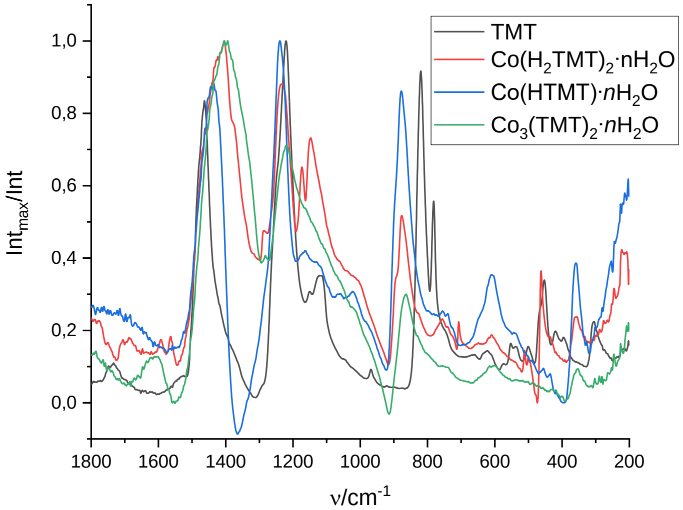

Fig. 1 Normalized FTIR spectra of TMT compounds with Co.

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Acknowledgements

Microgrant IDUB UW action IV.3.1.

Pt-loaded TiO_2 photocatalysts: Correlation between Schottky barrier height and photocatalytic performance

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The plasmonic properties of noble metals have the intriguing ability to catalyse chemical reactions in wide bandgap semiconductors such as titanium dioxide (TiO_2) when exposed to visible light [1-3]. The aim of the present study was to obtain plasmonic TiO_2+Pt solids with different Pt loadings from 0.5 to 2 wt% using the wet impregnation technique (TP corresponding to the pure TiO2 support, TP+0.5%Pt, TP+1%Pt and TP+2%Pt) and to investigate in detail how the increasing amount of deposited Pt affects the optical, electronic and catalytic properties of the TiO_2+Pt materials. Special attention was paid to X-ray photoelectron spectroscopy (XPS) to determine the height of the Schottky barrier (SB) in the prepared materials, which forms at the interface between Pt and TiO_2. The efficiency of the investigated catalysts in the photocatalytic degradation of bisphenol A (BPA) and coumarin dissolved in water was analysed in a batch slurry reactor system under visible light illumination.

The results of SEM-EDS analysis showed that the actual Pt loadings in the synthesised TiO_2+Pt catalysts corresponded to the nominal loadings. In addition, the results of XRD and TEM measurements showed that the morphology and crystallinity of the TiO_2 support were not affected during the wet impregnation process. The stability of the TiO_2 carrier was also confirmed by the results of the N_2-physisorption analysis, where the measured parameters were almost constant for all analysed solids. The average Pt particle size increased from 1.1 to 1.5 nm with increasing Pt content, which can be attributed to the clustering effect during wet impregnation. The UV-Vis DR spectra of the investigated TiO_2+Pt catalysts show that they can absorb light in the visible light range. The SB heights were 0.42 eV for TP+0.5%Pt, 0.34 eV for TP+1%Pt and 0.16 eV for the TP+2%Pt sample. The results of the time-correlated single photon counting (TCSPC) measurements show that the lifetime of the charge carriers in the investigated TP+Pt catalysts under visible light illumination is longer when the SB is lower, resulting in higher catalytic activity. Conversely, a higher SB shortens the lifetime of the "*hot electrons*" and reduces the catalytic performance. The results of the BPA degradation experiments show that regardless of the catalysts tested, no adsorption of BPA was observed in the dark phase. The observed degradation of BPA when using pure TP could be due to the presence of Ti^{3+} or surface defects in the TP. The TiO_2+Pt catalysts showed higher BPA degradation rates than the pure TP; moreover, the BPA degradation rates of the TiO_2+Pt catalysts increased with increasing Pt loading. Since different reactive ROS could be involved in heterogeneously catalysed BPA degradation, we also performed an experiment with coumarin (COUM) as a model pollutant. We measured the conversion of COUM dissolved in water to 7-hydroxycoumarin (7-HCOUM) by the reaction of COUM with the generated hydroxyl radicals (•OH). The results show that the amount of 7-HCOUM produced by the TiO_2+Pt catalysts upon illumination with visible light increases with decreasing Pt content and does not correspond to the order of BPA degradation rates. When the TiO_2+Pt catalyst is illuminated with visible light, the surface plasmon resonance effect of the Pt particles is triggered, which leads to the generation of "*hot electrons*" and holes (h^+) in the Pt particles. The generated "*hot electrons*" are transferred to the conduction band (CB) of TiO_2 after overcoming the SB at the interface between Pt and TiO_2. The results show that BPA reacts rapidly with superoxide anion radicals ($\cdot O_2^-$), so that their concentration is low, which favours the reduction of oxygen and the consumption of "*hot electrons*" (TiO_2 acts as an e^- sink). As a result, a high SB height leads to a low overall activity, as everything is determined by the transfer of "hot electrons" from the Pt particles to the TiO_2 CB. For COUM, it is the other way around: under the given experimental conditions, superoxide anion radicals ($\cdot O_2^-$), are slowly converted to hydroxyl radicals (•OH), so we have an excess of "*hot electrons*" on TiO_2 that want to return to the Pt particles. A high SBH value is favourable in the case of COUM oxidation, as it promotes the accumulation of "*hot electrons*" in the TiO_2 CB and hinders their recombination with h^+ in Pt.

The results of the study presented here show the complexity of heterogeneous photocatalysis when using TiO_2+Pt photocatalysts and illustrate that high catalytic activity is determined by the kinetics of the oxidation and reduction processes and the consumption of electrons and holes on the left or right side of the SB.

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Photocatalytic Reactor Design for Water Treatment: Organic Pollutant Degradation using 2-methyl-4-chlorophenoxyacetic acid (MCPA) as a Model Compound

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Photocatalytic technology has demonstrated broad potential in water treatment applications particularly for the degradation of organic pollutants[1]. Despite the potential, advancement of the technology is often slow as the majority of research focusses on materials synthesis. This work details the design of photocatalytic reactors optimised for water treatment, focusing on reactor configuration, photocatalyst selection/deployment, and maximising light source efficiency within the reactor. While photocatalyst material development has progressed significantly over the past 50 years, reactor design and upscaling has stalled, especially in relation to the Technology Readiness Level (TRL) scale. This study addresses these gaps by optimising reactor geometry, catalyst immobilisation, and light distribution, while emphasizing reactor sizing, mass transfer, and modelling for enhanced performance[2]. The primary objective is to create a sustainable, cost-effective solution for dealing with global water pollution challenges.

The initial work in this project has focussed on optimising the photocatalyst coating for deployment in a modular immobilised reactor. A low-cost spray gun method was utilised[3], replacing traditional sol-gel coating methods. Coating solutions comprised a 2% (w/v) P25 TiO_2 suspension with a SDS surfactant (sodium dodecylsulfate), sonicated at 50 kHz for 10 minutes, and sprayed onto a pre-treated 20 cm x 10 cm stainless steel plate, heated at 200° C to immobilise the catalysts. The reactor, modelled with Shapr 3D software, features a recirculation system, in-situ monitoring, and a reaction body. Gravity was used to accelerate the flow of contaminated water, containing MCPA as a model pollutant, over the surface of the photocatalyst coated plate, which was irradiated from above using UV LEDs (370nm). Following the photocatalytic treatment, the sample continued to flow over the sloping reactor plate into the collection pipe before returning to the reservoir tank. To monitor the reaction and determine its efficiency in real time, an amperometric flow cell electrochemical sensor was placed in the tank allowing real-time monitoring of the degradation of herbicide MCPA and the real-time data was transmitted by the sensor to the computer control system for analysis. The work presented here is an overview of this initial study demonstrating a robust and stable coating capable of efficient MCPA degradation under varying conditions.

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Characterization of PbS/C/PVDF-based Electrodes for CO2RR into HCOOH

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In our work, Electrodes of different types, based on thin PbS layers [1,2] and those constructed from nanoscale PbS powder, which was used to formulate easy-to-use pastes (slurry), were developed and characterized using SEM, XRD, EDS, XPS, and electrochemical techniques. All electrodes were supported by graphite as a conductive support and tested in a 0.5M K_2CO_3 electrolyte in the presence of CO_2.

The objective of this work was to develop electrodes capable of being used as cathodes to conduct electroreduction reactions of CO_2 to formic acid, while meeting certain key criteria such as high reaction current and low overvoltage, in order to approach the recommendations for application on a semi- and/or industrial scale.

we adopted an approach to pretreating our PbS/graphite electrodes with the aim of minimizing the parasitic hydrogen evolution reaction (HER) which can be described as follows:1)Perform linear voltammetry (LSV) from +1.5V to -2V vs. Ag/AgCl: This allowed us to identify the potential ranges for PbS reduction and CO_2 reduction; 2) Perform two voltammetric cycles from +1.5V to -2V: These cycles serve to precondition the electrode surface. We initiated the partial reduction of PbS to metallic lead Pb on the electrodes and 3) Perform chronoamperometry at -2V for 900s: By applying this reducing potential for a given time, we carried out the CO_2 reduction reaction while disfavoring the PbS to Pb reduction reaction and the HER-related reaction. Our strategy aimed to produce metallic lead Pb, which is very inactive in catalyzing the hydrogen release reaction. This partial reduction of PbS to Pb/graphite should reduce parasitic HER during CO_2 electroreduction.

By modifying the nature of the electrode surface to make it less active for HER, we have thus increased selectivity toward CO_2 reduction, as we initially intended.

The introduction of an activation step by in-situ reduction of PbS to metallic lead for HCOOH, coupled with favorable synergy and morphological restructuring, explains the highly active and selective behavior of the obtained electrodes.

Remarkable performance was obtained for electrodes formed on the base of PbS/C/PVDF-based paste with a 90/10 ratio, which constitute the best electrodes studied in this work. These findings pave the way for the development of scalable and energy-efficient CO_2 conversion systems that could be integrated into industrial processes or coupled with renewable energy sources, contributing to sustainable carbon utilization technologies.

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Acknowledgments

This work was completed thanks to the National Funds of Research, DGRSDT/MESRS (Algeria)

P-135

Design of Photocathodes Enhanced Properties for CO_2 photoelectroreduction using Pyramid/Nanowire Texturized Silicon coated with Naostructured PbS Thin Films

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Silicon-based photocathodes offer a promising avenue for photoelectrochemical CO_2 reduction (PEC CO2RR), a process that uses solar energy to convert CO_2 into valuable products. While Si itself is a promising material due to its narrow bandgap and high carrier mobility, its visible light absorption is limited. To enhance the efficiency and selectivity of PEC CO2RR on Si-based photocathodes, various strategies are employed, including Co-catalyst design and integration, nanostructuring and morphology, light absorption enhancement, and surface engineering. By optimizing these factors, the efficiency of converting solar energy into valuable products from CO_2 can be significantly improved. Control over the co-catalyst and surface properties can lead to a more selective production of desired products, such as HCOOH, or CH_3OH. Nanostructuring and surface engineering can enhance the stability of the photocathode under long-term operation.

This paper proposes an enhanced CO_2 electrochemical reduction reaction (CO2RR) by applying pyramid/nanowire textures to the silicon wafer. For pyramid formation, the etching process of the p-type (100) silicon wafers was accomplished and surveyed in a mixture of KOH and isopropyl alcohol solution [1]. In continuing, the MACE process with Ag was applied to the pre-formed pyramids to realize the Si nanowires [2]. The as-synthesized pyramids/Nanowires morphology presented a uniformity in shape and distribution. After that, nanostructured lead sulfide layers were deposited on the double-textured Si wafers [1,2]. Therefore, PbS-modified double texturization silicon electrodes were fabricated which will be used as photocathodes for the CO_2 electroreduction transformation. The results indicated that the double texturization of silicon substrates affected the amount of formation of the products issued from the CO2RR. This can be explained by the fact that the combined nanowire/pyramid structures significantly reduce the light reflection of the silicon substrate over a broad range in the visible spectrum allowing the formation of a large number of electrons that enter the CO2RR process in the presence of PbS as efficient co-catalyzer, used to trap the electrons and avoiding by the way the recombination of the formed electrons/holes couples issued from the light surface interaction. The combination of the pyramid/nanowire Si and PbS makes a promising texture to fabricate photocathodes suitable for application in photoelectrocatalytic synthesis.

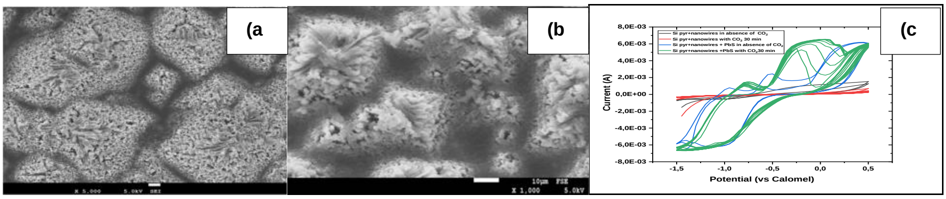

Fig.1. SEM picture (a) Before and (b) after nanostructured PbS thin film deposition on the double texturized Si substrate (c) Cyclic voltammetry curves of working electrodes fabricated with the double texturization (pyramids + Nanowires) Si without and with PbS nanoparticles, in the absence and in the presence of CO2 gas

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Acknowledgments

This work was completed thanks to the National Funds of Research, DGRSDT/MESRS (Algeria)

P-136

Cl-doped Polypyrrole for Photocatalytic Green Hydrogen Peroxide Production

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Hydrogen peroxide (H_2O_2) is a promising green oxidant for various industrial applications. However, its synthesis is primarily achieved through the environmentally costly anthraquinone process. Consequently, several alternative routes for eco-friendly H_2O_2 synthesis are under investigation. Photocatalytic H_2O_2 production via H_2O oxidation and O_2 reduction stands out as a sustainable option, as it generates no harmful by-products [1].

Conjugated polymers, as organic semiconductor have emerged as one of promising candidates for photocatalytic H_2O_2 generation active under visible light in recent years [2]. Here, we report a facile one step synthesis of Cl-doped polypyrrole (Cl-PPy) conjugated polymer via γ-radiolysis for photocatalytic H_2O_2 production. We investigated the effect of Cl doping on H_2O_2 production and studied various parameters (pH, light source, influence of oxygen, etc.) affecting H_2O_2 yield. Several analytical and characterization techniques were employed to understand the behavior of the Cl-PPy photocatalyst and its role in H_2O_2 generation. We found that Cl-PPy is highly active for photocatalytic H_2O_2 formation (2.9 mM/h) from H_2O and O_2 without any sacrificial agent, under UV-Vis illumination. Its higher photocatalytic activity, ease of synthesis, and recyclability confirms its potential for sustainable photocatalytic H_2O_2 production.

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P-137

Enhanced Photocatalytic Hydrogen Evolution via Optimized Coating Strategies for Photo Flow Reactors

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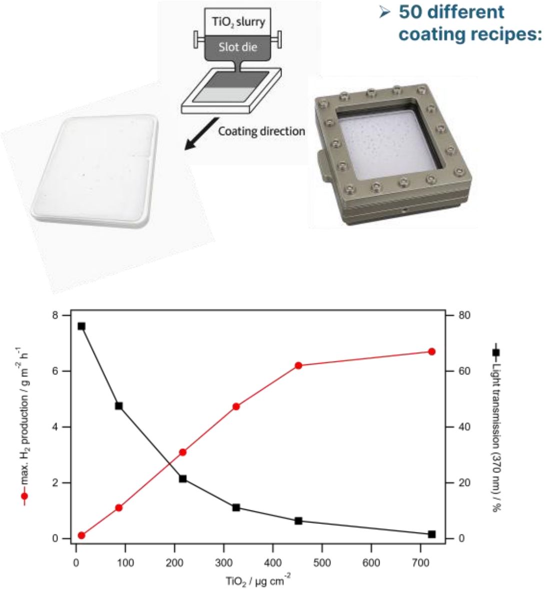
Photo flow reactors offer a scalable platform for continuous photochemical reactions by enhancing mass transfer, light distribution, and product removal compared to traditional batch systems. [1, 2] However, immobilizing semiconductor photocatalysts within these reactors remains a major challenge, especially for hydrogen evolution applications, where catalyst adhesion, stability, and light absorption must be finely balanced. In this study, we systematically optimized slot-die coated anatase TiO_2 films for photo flow reactor operation under 370 nm UV light.

By incorporating colloidal SiO_2 (2.5 µL mL^{-1}) to enhance porosity and $CaCl_2$ (0.6 mg mL^{-1}) to improve adhesion via ionic crosslinking, we achieved uniform, mechanically stable coatings with a TiO_2 loading of 723 µg cm^{-2}, yielding UV transmittance between 1.5–6%. The coatings, post-functionalized with 0.01 mg cm^{-2} Pt by photodeposition, demonstrated hydrogen production rates of 7.37 g m^{-2} h^{-1} in continuous flow, corresponding to a quantum efficiency of 65%. Long-term operation over 100 hours resulted in a stable productivity of 5.25 g m^{-2} h^{-1} (QE = 47%), highlighting the durability of the optimized system.

Furthermore, productivity per unit TiO_2 mass peaked at 0.89 g H_2 g^{-1} TiO_2 h^{-1} with a catalyst loading of 325 µg cm^{-2}, revealing a trade-off between catalyst density and mass-specific activity. These findings underline the importance of controlling coating thickness, porosity, and light absorption properties to maximize efficiency in photo flow reactors, offering a robust strategy for scalable hydrogen generation by semiconductor photocatalysis.



➢ 50 different coating recipes:

Fig. 1. HER catalyst activity and light transmission relative to the mass of TiO_2 coating.

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This work has received financial support from the Austrian Research Promotion Agency FFG.

P-138

Modeling and Simulation of Decorated Graphene Oxide for Photocatalytic Generation of Hydrogen

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Over recent decades, global energy demand has relentlessly increased, driven by industrialization and urbanization, leading to heightened environmental pollution [1]. Recognized as pivotal for sustainable economic development and societal prosperity, energy usage has predominantly relied on traditional fossil fuels. However, the combustion of these fuels releases approximately 7.8 billion metric tons of CO2 annually, alongside other harmful gases such as CH4, SO2, and NH3, exacerbating issues like global warming.

Hydrogen (H2) is utilized as an auxiliary fuel source due to its high energy content per unit weight (122 kJ/g). Notably, the energy yield of hydrogen is approximately 2.75 times greater than that of hydrocarbon fuels [2]. Additionally, hydrogen is regarded as an exceptionally clean energy source, as it produces only water upon combustion, thereby emitting no harmful gases like CO2 that contribute to global warming. Biological methods of hydrogen production include biophotolysis, dark fermentation, photo-fermentation, integrated fermentation, and artificial photosynthesis.

Photocatalytic water splitting is considered one of the most promising methods for converting water into H2 and O2. It involves employing a semiconductor photocatalyst to harness solar energy. This approach is appealing due to the abundance, cleanliness, and renewability of sunlight. Additionally, it offers economic viability and simplicity in execution [3].

A wide array of photocatalysts have been explored for this process, including TiO2, ZnO, ZnS, NaTaO3, WO3, MoO3, phosphides, sulphides, chalcogenides, transition metal carbides, among others [4]. Conventional photocatalysts such as TiO2, ZnO, and ZnS have been extensively researched in the past. However, due to their large band gap (~3.2 eV), they are now being superseded by other types of photocatalysts, including metal-free catalysts such as carbon-based nanomaterials. Alongside possessing a smaller band gap, carbon-based nanomaterials exhibit unique morphologies, controlled structures, and are non-toxic.

My research focuses on graphene oxide (GO), reduced graphene oxide (RGO), and cesium-decorated reduced graphene oxide (CsRGO) to determine whether CsRGO can serve as an efficient photocatalyst and how to improve its performance. In this study, I employ Density Functional Theory (DFT) as implemented in the Quantum ESPRESSO code to investigate the structural, electronic, and optical properties of GO, RGO, and CsRGO compounds for photocatalytic applications.

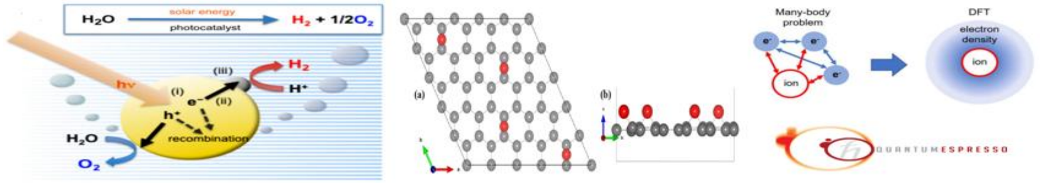

Fig. 1. Illustration of Photocatalytic Water Splitting on Decorated Graphene Oxide with DFT Simulations.

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Acknowledgements

This work was funded by the German Academic Exchange Service (DAAD) under the ERA Fellowships – Green Hydrogen program.

$TiO_2/ZnGa_2O_4:Cr^{3+}/Pt$ composite for high-efficiency photocatalytic hydrogen production

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Hydrogen has garnered significant attention as a clean, renewable energy source that offers a promising alternative to fossil fuel dependency and environmental degradation. The photocatalytic production of hydrogen is a very attractive strategy [1]. TiO_2 is frequently used as a photocatalyst due to its low cost, chemical stability, and robustness under UV illumination. Nevertheless, its high bandgap energy (3.2 eV) restricts excitation to UV light, and the rapid recombination of photogenerated electron-hole pairs limits photon-to-charge conversion efficiency. One strategy to enhance photocatalytic performance is doping with noble metals (e.g., Pt, Au, Ag, Pd), which improves charge separation, extends light absorption through the surface plasmon resonance effect, and increases surface reactivity [2]. Additionally, persistent luminescent materials show potential in prolonging photocatalytic activity after ceasing light irradiation, thus enhancing energy conservation. Chromium (Cr^{3+})-doped persistent luminescent nanoparticles (PLNPs), such as $ZnGa_2O_4:Cr^{3+}$ (ZGO), are notable for their prolonged near-infrared emission and efficient energy transfer mechanisms [3]. Although some studies have explored PLNPs in photocatalysis, they have mainly focused on degrading dyes and organic contaminants. Thus, in this work, we design a novel photocatalyst composed of TiO_2, $ZnGa_2O_4:Cr^{3+}$, and Pt for the production of green hydrogen via triethanolamine photoreforming, using commercial TiO_2 P25 as a reference.

XRD analysis confirmed high crystallinity and phase purity. SEM images revealed that the TiO_2 surface was uniformly covered by $ZnGa_2O_4:Cr^{3+}$ nanoparticles with diameters ranging from 2 to 27 nm. TEM images and STEM-EDS showed close contact among the particles, indicating the formation of a heterojunction. Optical characterizations via UV–Vis diffuse reflectance spectroscopy revealed enhanced visible-range absorption for materials containing Pt. Hydrogen evolution was evaluated using a Peschl Ultraviolet photoreactor with UV medium-pressure lamps as the irradiation source. As shown in Fig. 1, when comparing synthesized TiO_2, $TiO_2/ZnGa_2O_4:Cr^{3+}$, pure $ZnGa_2O_4:Cr^{3+}$, commercial P25, and $P25/ZnGa_2O_4:Cr^{3+}$, commercial P25 exhibited the highest hydrogen evolution. However, upon incorporating of Pt, materials with our synthesized TiO_2 showed enhanced efficiency relative to those with commercial P25. Notably, the composite $TiO_2/ZnGa_2O_4:Cr^{3+}/Pt$ displayed considerably higher hydrogen generation after 4 h, suggesting a strong synergistic effect among these materials. Although an increased hydrogen production was expected post-irradiation, the results are promising compared to commercial TiO_2, and further improvements to the photocatalyst will be pursued. Thus, this work introduces a novel approach to designing photocatalysts that incorporate persistent luminescent materials, achieving high efficiency in photocatalytic hydrogen evolution.

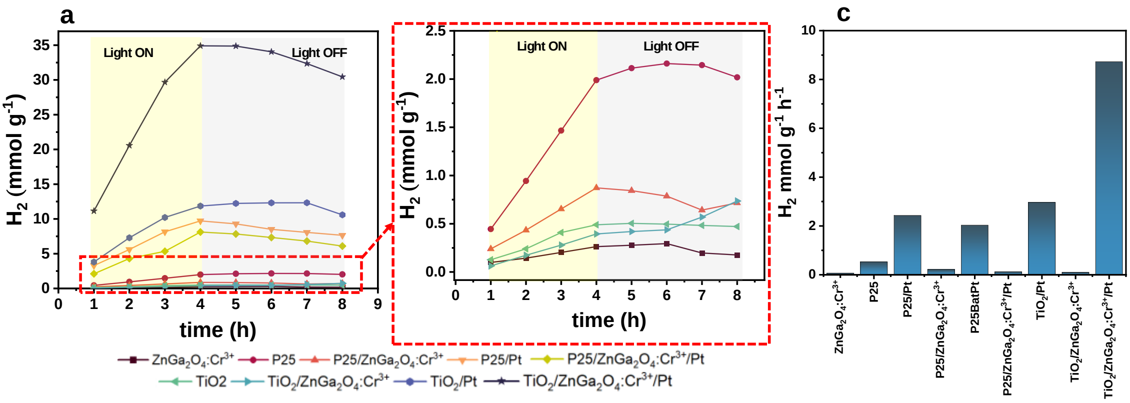

Fig. 1. a) Photocatalytic hydrogen evolution; b) Average hydrogen evolution per hour.

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Acknowledgements

This work received financial support from Human Resource Program of the Brazilian National Agency for Petroleum, Natural Gas, and Biofuels – PRH-ANP 49 (grant 045919) and FAPESP (grants # 2024/18336-0, 2024/07730-9, 2023/14930-1).

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