The 28th International Conference
on

Semiconductor Photocatalysis and Solar Energy Conversion
(SPASEC-28)

The 29th International Conference
on

Advanced Oxidation Technologies for Treatment of Water, Air and Soil
(AOTs-29)

ABSTRACTS

Sponsor

RTI Redox Technologies, Inc.

BRNO
UNIVERSITY
OF TECHNOLOGY

Brno University of Technology, Czech Republic
May 12 – 15, 2025

Executive Organizing Committee of SPASEC-28 & AOTs-29

Dr. Hussain Al-Ekabi, (Lead Conference Organizer), Redox Technologies Inc., Canada
Professor Petr Dzik (Co-chair), Brno University of Technology, Czech Republic
Professor Michal Vesely (Co-chair), Brno University of Technology, Czech Republic

Local Organizing Committee of SPASEC-28 & AOTs-29

Dr. Jiri Smilek (Chair, Local Organizing Committee), Brno University of Technology, Czech Republic
Mrs.Vendula Hrabalova, Brno University of Technology, Czech Republic
Dr. Xenie Kourilova, Brno University of Technology, Czech Republic
Dr. Jitka Krouska, Brno University of Technology, Czech Republic
Mr. Jan Pernica, Brno University of Technology, Czech Republic

International Scientific Committee of SPASEC-28 & AOTs-29

Professor Salah S. Al-Zubaidi, University of Baghdad, Iraq
Professor Detlef Bahnemann, Leibniz Universitat Hannover, Germany
Dr. Beatriz Trindade Barrocas, Universidade de Lisboa, Portugal
Professor Miran Čeh, Jozef Stefan Institute, Slovenia
Professor Siegfried Denys, Antwerp University, Belgium
Professor Şifa Doğan, Cyprus International University, Turkish Republic of Northern Cyprus
Professor Dana Dvoranová, Slovak Technical University, Bratislava, Slovak Republic
Professor Petr Dzik, Brno University of Technology, Czech Republic
Professor Zeynep Eren, Atatürk Üniversitesi, Turkey
Professor Parag R Gogate, Institute of Chemical Technology, Mumbai, India
Professor Chantal Guillard, IRCELYON, University Lyon, University Claude Bernard, France
Professor Seigo Ito, University of Hyogo, Japan

Professor Ladislav Kavan, J. Heyrovsky Institute of Physical Chemistry, Czech Republic
Professor Štěpán Kment, Palacký University Olomouc, Czech Republic
Professor Ewa Kowalska, Jagiellonian University, Poland
Professor Josef Krýsa, University of Chemistry and Technology Prague, Czech Republic
Dr. Hana Krýsová, J. Heyrovsky Institute of Physical Chemistry, Czech Republic
Professor Pavel Krystynik, J.E.Purkyne University in Usti nad Labem
Professor Yao-Tung Lin, National Chung Hsing University, Taiwan
Professor Claudio Minero, Turin University, Italy
Professor Guido Mul, University of Twente, The Netherland
Professor Kevin O'shea, Florida International University, USA
Professor Albin Pintar, National Institute of Chemistry, Ljubljana, Slovenia
Professor Xie Quan, Dalian University of Technology, China
Dr. Jan Prochazka, President, Czech Society for Applied Photocatalysis (CSAP), Czech Republic
Professor Christian Schoneich, University of Kansas, USA
Professor Chiaki Terashima, Tokyo University of Science, Japan
Professor Sammy Verbruggen, Antwerp University, Belgium
Professor Michal Vesely, Brno University of Technology, Czech Republic
Professor Michael Wark, University Oldenburg, Germany
Professor Shujuan Zhang, Nanjing University, China

Table of Contents

SESSION I

SESSION II

SESSION III

SESSION IV

SESSION V

SESSION VI

SESSION VII

SESSION VIII

SESSION IX: PFAS Oxidative Treatment

SESSION X

SESSION XI

SESSION I

Photoelectrochemical and photoelectrosynthetic reactions on n-type semiconductor photoelectrodes

T. Imrich, M. Neumann-Spallart, J. Krýsa*
Department of Inorganic Technology, University of Chemistry and Technology Prague,
Technická 5, 166 28 Praha 6, Czech Republic, E-mail: josef.krysa@vscht.cz

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.

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) [1]. Fe_2TiO_5 is a medium-wide bandgap ($E_g = 2.1$ eV) [2] 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 standard photoelectrochemical oxidation reactions involving valence band processes on some oxide semiconductors and to compare them with those observed on TiO_2 and WO_3. The first case study was the photoelectrochemical oxidation of model organic pollutants dissolved in water as dyes, herbicides, etc. [3]. The second case study analyses Br^- oxidation on Fe_2TiO_5 and α-Fe_2O_3 and seeks to understand how differences in the efficiencies of the four tested semiconductors can be attributed to their valence band positions and the redox properties of the solute [4].

References:

[1] J. H. Kennedy, K.W. Frese, *J. Electrochem. Soc*. 125, 709 (1978).
[2] T. Imrich, H. Krýsová, M. Neumann-Spallart, J. Krýsa, *Catal. Today* 413–415, 113892 (2023).
[3] T. Imrich, M. Neumann-Spallart, J. Krýsa, *Photochem. Photobiol. Sci*. 22, 419–426 (2023).
[4] T. Imrich, M. Neumann-Spallart, J. Krýsa, *Catal. Today* 432, 114627 (2024).

Acknowledgements:

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

Photocatalytic Air Treatment: Potentials and Limitations

Detlef Bahnemann

Laboratory “Photoactive Nanocomposite Materials”
Saint-Petersburg State University, Russia,
e-mail: detlef.bahnemann@spbu.ru

Due to the increased emission of nitrogen oxides (NO_x) from flue gas and its high polluting effects on human health and the ecosystem, much attention is directed toward NO_x monitoring, removal, and control. This lecture reviews the latest progress in NO_x photocatalytic removal emphasizing the advancements in surface/interface engineering of photocatalytic materials considering the reaction mechanism and modifications for controlling the generation of toxic intermediates. Defect chemistry, facet controlling, and stability of the photocatalytic systems are comprehensively discussed. The challenges/bottlenecks of the practical applications are also highlighted. Indeed, the photocatalytic removal of NO_x is still a significant challenge due to the remaining limitations. Herein, the state-of-the-art in utilizing widely used semiconducting materials such as TiO_2 and g-C_3N_4-based photocatalysts are summarized, focusing on the eminent strategies to amend their performances under visible light. Also, the utilization of MOFs for NO_x photoreduction is discussed highlighting the importance of the coincidence of the organic linkers acting as light sensitizers and the metallic nodes to intensify the transfer of photoinduced electrons. In addition to the concerns mentioned above, so far, no serious consideration has been paid to the control of toxic by-products and intermediate species generation through NO_x removal methodologies. Moreover, some perspectives will be discussed regarding the advanced pathways to develop novel efficient nanomaterials for the removal of NO_x hazards from the environment.

References:

B. Rhimi, M. Padervand, H. Jouini, S. Ghasemi, D. W. Bahnemann, C. Wang

“Recent Progress in NO_x Photocatalytic Removal: Surface/Interface Engineering and Mechanistic Understanding”, J. Environ. Chem. Eng. 10 (2022) Article Number 108566 (24p)

Application of High Entropy Alloys in (Photo)(Electro)Catalytic Degradation of Antibiotics

Lara Einfalt[1,2], Barbara Ljubec Božiček[1,2], Belisa Alcantara Marinho[1], Miran Čeh[1,*]
[1]Department for Nanostructured Materials, Jožef Stefan Institute, Ljubljana, Slovenia.
[2]Jožef Stefan International Postgraduate School, Ljubljana, Slovenia.
(*miran.ceh@ijs.si)

Photocatalytic oxidation offers an efficient and sustainable method to break down antibiotics in wastewater into harmless by-products. This process relies on the production of highly reactive species such as (-OH) radicals, superoxide radicals ($O_2^{\bullet-}$, $HO_2^{\bullet}$) or other reactive species [1]. The combination of photocatalysis and electrochemistry has led to the development of photoelectrocatalysis (PEC), a promising technology for environmental remediation. Although traditional catalysts, such as TiO_2 and ZnO are widely used, high-entropy materials (HEMs) have recently attracted attention for their unique catalytic properties [2].

These materials, composed of five or more elements randomly distributed in a single-phase lattice, exhibit lattice distortions and uneven electron distribution between metals of different valences and oxygen vacancies in the case of HEO [3]. These features may enhance catalytic reactions, positioning HEMs as a promising new approach for wastewater treatment. This is why, in our work, we report on the use of a high-entropy alloy (HEA) with composition TaNbHfZrTi in test studies for tetracycline degradation. TaNbHfZrTi HEA disks with $\Phi = 20$ mm were anodized using a two-electrode system in an electrochemical cell at 10-60 V for 2 h. The electrolyte for anodization contained 75 vol. % glycerol, 25 vol. % deionized water, and 0.25 M NH_4F. After anodizing, the discs were annealed for 1 hour in air at temperatures between 250 and 1000 °C in a muffle furnace. The nanotubular oxide layers were then analyzed by scanning electron microscopy, Raman spectroscopy, and UV-Vis spectrophotometry. Anodized discs were then used for photocatalytic and photoelectrocatalytic degradation of tetracycline (TC) at a concentration of 10 mg/L using different experimental conditions.

Collected samples and their degradation rate were measured with UPLC-PDA. The results show that the outer diameter of the nanotubes increased from 25 ± 1.2 nm to 140 ± 1.3 nm with increasing anodization voltage from 10 V to 60 V. Raman spectroscopy revealed that the oxide film on the substrate transitioned to a crystalline structure after annealing at 1000°C. However, the amorphous structure observed at lower annealing temperatures did not affect the degradation efficiency of the film. Interestingly, samples annealed at lower temperatures showed improved photocatalytic efficiency for TC degradation. In particular, film annealed at 250°C achieved 60 % degradation after one hour. The PEC performance of samples annealed at 250 °C showed a clear relationship with voltage, with higher voltages consistently resulting in better efficiencies. After 3 hours of PEC degradation of TC, efficiencies of 82 % were achieved at 12 V and 10 V, dropping slightly to 80 % at 8 V and further to 63 % at 6 V. In reuse tests conducted at 4 V, the efficiency started at 42 % and showed a marked improvement, reaching 86 % in the fourth cycle, ultimately enhancing the material's durability. Further research will aim to identify the strategies to improve the efficiency of the film even further. It was concluded that TaNbHfZrTi HEA and possibly similar compositions in metallic or oxides form exhibit potential as photo- and photoelectrocatalysts for removing not only antibiotics from water but also organic pollutants.

References:

[1] Wang J. & Zhuan R. (2020). Science of The Total Environment, 701, 135023.
[2] Wang L., Zhao J., Liu H. & Huang J. J (2018). Taiwan Inst Chem Eng, 93, 590–602.
[3] Wang D., Liu Z., et al., (2019). J. Mater. Chem. A., 7, 24211–24216.

Acknowledgments:

The authors gratefully acknowledge the Slovenian Research Agency (ARIS) for financial support within the research program P2-0084 and project PR-11484. This work has also received funding from the European Union's Horizon research and innovation program under the HORIZON-WIDERA-2022-TALENTS-02 grant agreement No. 101090289.

SESSION II

Redox Mediators for Dye-Senstized Solar Cells

Ladislav Kavan
J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences,
Dolejskova 2155/3, 182 00 Prague 8, Czech Republic
E-mail: kavan@jh-inst.cas.cz

The dye-sensitized solar cell (DSSC) has been a subject of tremendous scientific and industrial efforts during the last three decades [1-4]. Key recent discoveries include a successful replacement of the traditional iodine-based redox mediator by the Co(III/II) [5], and particularly Cu(II/I) redox couples [2, 6, 7]. The champion DSSC, presented in 2023 by Ren et al. [2], employed the TiO_2 (anatase) photoanode sensitized by two self-organized dyes, which were interfaced to a Cu(II/I)-based redox mediator. This device provided under the AM 1.5G solar light the world-record conversion efficiency of 15.2%, the open-circuit photovoltage (V_{OC}) of 1.04 V and the fill factor of 82.1 [2]. These impressive parameters are comparable to those of the common perovskite solar cells. Yet, there is still a space for improvements. The mediator, which was used in the champion device, was $Cu^{II/I}(tmby)_2(TFSI)_{2/1}$; tmby is 4,4', 6,6-tetramethyl-2,2'-bipyridine, and TFSI is bis(trifluoromethylsulfonyl)imide. An issue is the organic base additive, which is commonly used in almost all the electrolyte solutions for DSSCs. These additives are usually derivatives of pyridine [8], but various imidazoles (such as 5-chloro-1-ethyl-2-methyl-imidazole (CEMI)) were recently used, too [2, 9].

They enhance the V_{OC} by upshifting the conduction band minimum (CBM) of titania photoanode through a collective influence of: (i) blocking of the undercoordinated Ti-atoms atoms at the surface, (ii) decrease of the concentration of potential- determining cations (H^+ or Li^+) at the TiO_2 surface and (iii) formation of dipole moment through the Ti…N bonds. In addition, however, the N-containing heterocycles do react with tetracoordinated Cu (II/I)-bipyridine complexes, used as redox mediators. The experimental electrochemical potentials of $Cu(tmby)_2^{2+/+}$ in the CEMI-modified electrolyte solution, interrelated with the respective values of the flatband potentials (Fermi level positions) in TiO_2 [10]provide an estimate of the maximum accessible open-circuit photovoltage of DSSC to be 1.55 V. If we neglect the other inherent loses of solar cells, this value is the benchmark for future optimization of these solar cells. The ideal additive should keep up the positive effects of N-heterocycles (e.g., the Fermi level upshift in TiO_2), but without changing the mediator's redox potential.

References:

[1] A. Hagfeldt, et al., Chem. Rev, 110 (2010) 6595-6663.
[2] Y. Ren, et al., Nature, 613 (2023) 60-65.
[3] L. Kavan, J. Solid State Electrochem., 28 (2024) 829-845.
[4] L. Kavan, Curr. Opinion Electrochem, 2 (2017) 88-96.
[5] J.H. Yum, et al., Nat Commun, 3 (2012) 631.
[6] L. Kavan, et al., Electrochim. Acta, 227 (2017) 194-202.
[7] Y. Saygili, et al., J. Am. Chem. Soc, 138 (2016) 15087-15096.
[8] P. Ferdowsi, et al., Electrochim Acta, 265 (2018) 194-201.
[9] D. Zhang, et al., Nat Commun, 12 (2021) 1777.
[10] V. Mansfeldova, et al., J. Phys. Chem. C, 125 (2021) 1902-1912.

Indirect Techniques of EPR Spectroscopy in Heterogeneous (Photo)Catalysis

D. Dvoranová*, Z. Dyrčíková, M. Malček Šimunková, K. Lušpai
Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic
(*dana.dvoranova@stuba.sk)

The electron paramagnetic resonance (EPR) spectroscopy represents unique sensitive spectroscopic method that allows detection and characterization of various paramagnetic species. Thus, the EPR provides direct detection of free radicals, utilization of indirect techniques, such spin trapping, spin scavenging, oxidation of sterically hindered amines or photoreduction, is often applied, *e.g.* in the heterogenous (photo)catalysis. These indirect techniques allow detection of transient intermediates (hydroxyl radical, superoxide radical anion, singlet oxygen, sulphate radical, *etc*.) and help to understand the ongoing radical processes. Due to the better availability of cw-EPR spectrometers, the interest in EPR spectroscopy, which nowadays celebrates its 80th birthday, as an additional analytical method for the determination and identification of paramagnetic species has rapidly increased. The key factors for the successful application of these techniques in the characterization of (photo)activity of studied materials are the careful selection of the experimental conditions and a precise analysis of the experimental EPR spectra. The deeper view on these techniques, their application and pointing on their pros and cons will be discussed. [1-6]

Acknowledgment:
This study was financially supported by the Slovak Research and Development Agency under the contracts DS-FR-22-0011 and No. APVV-21-0039 and Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0422/24).

References:

[1] Barbieriková Z., Dvoranová D., Brezová V. (2021) Chapter 8, *Materials Science in Photocatalysis*, Elsevier, Netherlands.
[2] Dvoranová D., Barbieriková Z., Brezová V. (2014) *Molecules* 19, 17279-17304.
[3] Tobaldi D. M., Dvoranová D., Lajaunie L., et al. (2021) *Chemical Engineering Journal* 405, 126651.
[4] Nikšić V., Malček Šimunková M., Dyrčíková Z., et al. (2024) *Optical Materials* 152, 115454.
[5] Atri, S., et al. (2024) *Chemical Engineering Journal* 502*,* 157814.
[6] Atri, S., et al. (2024) *Nanoscale* 16, 18430.

Innovative supported photocatalysts for solar-driven environmental remediation: From lab innovations to real-world applications

B. Trindade Barrocas[1],*, A.C. Marques[1], M. Conceição Oliveira[2]

[1]CERENA, Department of Chemical Engineering (DEQ), Instituto Superior Técnico, Universidade de Lisboa, Portugal

[2]CQE, Department of Chemical Engineering (DEQ), Instituto Superior Técnico, Universidade de Lisboa, Portugal

(**beatriz.trindade.barrocas@tecnico.ulisboa.pt*)

The growing challenges of climate change, pollution, and water scarcity demand innovative and sustainable solutions. Water contamination by persistent organic pollutants, including pharmaceuticals, is a critical issue, as these substances are often resistant to conventional treatment methods. Heterogeneous photocatalysis, particularly when driven by solar energy, offers a promising alternative due to its cost-effectiveness, high efficiency, and environmentally friendly approach.

In this study, we explore advanced supported photocatalysts based on semiconductor nanomaterials immobilized on porous silica-titania microspheres (MICROSCAFS®). These materials provide a robust scaffold that enhances photocatalyst stability, prevents nanoparticle aggregation, and facilitates easy recovery and reuse.

The MICROSCAFS® were prepared via a modified sol-gel method, integrating polymerization-induced phase separation to achieve controlled meso- and macroporosity. These tailored microstructures significantly influence photocatalytic performance, as demonstrated in the degradation of minocycline (a widely used antibiotic) and a real wastewater from a Portuguese pharmaceutical industry under simulated solar irradiation. The photocatalysts exhibited complete minocycline degradation, within 30 min of solar irradiation.

Beyond model pollutants, we extended our study to real wastewater samples from a pharmaceutical industry, assessing transformation products via high-resolution mass spectrometry and in-silico toxicity analysis. Photocatalytic tests on the real wastewater confirmed the system's effectiveness, achieving 100% degradation of minocycline and by-products within 30 and 120 minutes of irradiation, respectively. The results confirmed the generation of less toxic by-products, indicating the potential for safer water discharge.

Our findings highlight the potential of MICROSCAFS®-supported photocatalysts as versatile and scalable solutions for wastewater purification and resource recovery, paving the way for sustainable environmental remediation strategies.

References:

[1] Fernandes, S.M., Barrocas, B.T., Nardeli, J.V., Montemor, M.F., Maçôas, E., Oliveira, M.C., Carvalho, C.C.R., Lauria, A., Niederberger, M., & Marques, A.C. (2024). *Journal of Environmental Chemical Engineering*, 12(2), 112043.

[2] Fernandes, S.M., Barrocas, B.T., Vale, M., Oliveira, M.C., Mohtar, A.A., & Marques, A.C. (2025). MICROSCAFS® for minocycline elimination from water and real wastewater: Porosity and TiO_2 nanoparticles effect. *Chemical Engineering Journal*, 504, 158771.

Acknowledgements:

The authors gratefully acknowledge the support of CERENA (FCT-UIDB/04028/2025 and FCT-UIDP/04028/2025), the FCT project SOLAR2CLEAN - Engineered solar light driven photocatalytic systems for wastewater purification (http://doi.org/10.54499/PTDC/EQU-EQU/1056/2020), as well as the project RNEM-LISBOA-01–0145-FEDER-022125-IST, Centro de Química Estrutural (UIDB/00100/2020 and UIDP/00100/2020) and Institute of Molecular Sciences (LA/P/0056/2020).

SESSION III

Green Sol-gel Synthesis of TiO_2, SiO_2, and ZnO Based Photocatalytic Coatings for Environmental Cleanup

M. Ayyaz*, B. Aksu, M.P. Pedeferri, M.V. Diamanti
Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Italy.
(*muhammad.ayyaz@polimi.it)

Photocatalytic coatings have gained huge attention for environmental cleanup, especially in air and water purification. Current research is focused on developing an eco-friendly and sustainable synthesis approach for TiO_2, SiO_2, and ZnO based photocatalytic coatings using sol-gel and dip-coating technique. Distilled water, acetic acid, and oxide precursors only, were used in synthesis to avoid hazardous solvents and to ensure a green synthesis route. The influence of aging time, synthesis temperature and deposition conditions were systematically evaluated to optimize the coatings for improved photocatalytic performance. The TiO_2 sol was prepared at room temperature, 40°C, and 50°C to study the effects of temperature over its stability and photocatalytic efficiency; SiO_2 and ZnO sols were prepared at room temperature. The final sols were coated over 2.5×2.5 cm^2 glass substrate by single and multilayer dipping. Each coated layer was post-annealed at 400°C prior to further deposition. However, SiO_2 layers were dried at room temperature prior to deposit further layers. The stability of the sols over aging was evaluated by dynamic light scattering (DLS). The finally prepared coatings were characterized by x-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and field emission scanning electron microscope (FE-SEM) for structural and morphological evaluation. The photocatalytic ability of coatings was tested by photodegradation of rhodamine B (RhB) dye under UV (λ = 365 nm) and visible light irradiance.

DLS study of TiO_2 sol revealed nanoparticles formation (10 - 100 nm) with increasing sizes over aging, indicating particles growth and colloidal instability. XRD confirmed the presence of pure anatase phased TiO_2 nanoparticles with major peak (101) at 25.30° and average crystallite size of 5 nm while formation of crystalline ZnO was confirmed by (100) phase with average crystallite size of 23 nm []. EDS also confirmed the elemental composition of all coatings. FE-SEM revealed a crack-less and uniform morphology of SiO_2-TiO_2 coatings among all other coatings. The interlayer of SiO_2 improved TiO_2 dispersion and adhesion over glass substrate by reducing the interfacial stress.

The SiO_2-TiO_2 coatings showed 100% photocatalytic degradation of RhB under UV irradiance with kinetic constant of 0.0127 min^{-1}, while TiO_2 coatings showed 92% degradation with a rate constant of 0.0102 min^{-1}. The porous nature of SiO_2 enabled better dispersion of TiO_2 with higher active surface area and prevented agglomeration and delamination during photocatalytic reactions which directly improved the photocatalysis efficiency of coatings. The heating effect also accelerated hydrolysis and resulted in production of larger number of crystallites in TiO_2 sol which improved its photocatalytic efficiency. ZnO showed 36% degradation with a rate constant of 0.0013 min^{-1}, SiO_2-ZnO showed 49% with a rate constant of 0.0019 min^{-1}), and TiO_2-ZnO showed 62% with a rate constant of 0.0037 min^{-1}). In visible driven photocatalysis only ZnO coating showed 56% degradation with a rate constant of 0.0025 min^{-1}, while other coatings do not show significant degradation.

Overall, this research contributes to the development of efficient photocatalytic coatings for environmental applications. Further optimization of sol formulations, deposition and testing conditions could improve the performance of these materials in real-world applications.

TiO_2 Thin Films for Photo-, Electro- and Photoelectroactivity Degradation of Tetracycline

Lara Einfalt[1,2,*], Barbara Ljubec Božiček[1,2], Belisa Alcantara Marinho[1], Miran Čeh[1]
[1]Department for Nanostructured Materials, Jožef Stefan Institute, Ljubljana, Slovenia.
[2]Jožef Stefan International Postgraduate School, Ljubljana, Slovenia.
(*lara.einfalt@ijs.si)

Titanium dioxide TiO_2, available in various morphologies, effectively breaks down organic pollutants in wastewater when exposed to UV light and/or electric current, converting them into more environmentally friendly compounds. One approach to synthesize TiO_2 nanotubes is to use an anodic oxidation process of titanium metal foils, which is a relatively simple, inexpensive, and straightforward procedure. In addition, anodically grown nanotube-shaped TiO_2 layers have improved charge separation due to the possibility of unidirectional charge transport along the nanotube walls and inhibit the recombination of the photogenerated electron-hole pairs [1].

The anodic oxidation process also allows precise control of the thickness and morphology of TiO_2 nanotubes by varying anodizing parameters such as applied voltage, duration of the anodic oxidation process, electrolyte composition, and solution temperature [2]. The as-anodized TiO_2 nanotubes are initially amorphous and require transformation to the anatase crystalline phase by thermal annealing to exhibit photocatalytic activity [3,4]. With this in mind, our work aims to explore the synthesis of anodically grown TiO_2 layers on titanium foil and to evaluate their potential catalytic application in antibiotic tetracycline (TC) degradation. To synthesize TiO_2 nanotubes, titanium foils (200 µm thick) were cut into 2.4×2.4, 3.6×3.6 and 4.6×4.6 cm square shaped foils and ultrasonically cleaned in ethanol and water. The foils were anodized at a constant potential of 60 V for 3 h in ethylene glycol electrolyte containing 0.3 wt. % NH_4F and 2 vol. % deionized waters at an exposed surface area of 1, 5, and 10 cm^2.

The foils were then annealed in air at 450 °C for 1 hour, to transform the initially amorphous TiO_2 nanotubes into polycrystalline anatase TiO_2. The synthesized nanotubular TiO_2 layers were then characterized by scanning electron microscopy (Verios 4G HP, Thermo Fisher) and evaluated for their photo-, electro-, and photoelectrocatalytic activity for the degradation of TC (10 mg/L) in a custom-made photoelectroreactor (APRIA Systems). Samples were collected at defined intervals for up to 60 minutes and analysed by UPLC-PDA at 357 nm (Waters ACQUITY I-Class). Catalytic experiments were carried out at various voltages to evaluate the performance of catalyst under different conditions. For photocatalysis, the highest degradation was observed at a flow rate of 1500 mL/min and with the samples with the largest exposed surface (10 cm^2). The film's reuse did not impact performance. The electrocatalytic degradation process showed the highest efficiency at 12 V (59 %) and 4 V (52 %), with 4 V chosen for further experiments due to its lower energy consumption. The addition of different concentrations of NaCl improved the degradation performance by facilitating the generation of strong oxidative species and increasing ionic conductivity, with a peak efficiency of 78 % at 100 mg/L NaCl.

Reuse of the films on a 1 cm^2 surface area improved degradation rates from 25 % to 71 %, while larger surface areas (5-10 cm^2) maintained efficiencies of 65-70 %. Future work will focus on further optimizing these parameters. In addition, evaluating the reusability and stability of nanotubular films is essential to advance their application in environmental remediation.

References:

[1] Thavasi V., et al., (2009). Materials Science and Engineering: R: Reports, 63, 81–99.
[2] Zakir O., et al., (2023). Journal of Solid-State Electrochemistry, 27, 2289–2307.
[3] Macak J.M., et al., (2007). Curr Opin Solid State Mater Sci, 11, 3–18.
[4] Wang C., et al., (2023). J Photochem Photobiol a Chem, 437, 114475.

Acknowledgments:

Slovenian Research Agency (ARIS) financially supported this work within the research program P2-0084 and projects L2-2614, PR-10415 and J2-3051.

Plasma Modification of Bio-Inspired Nanofibers for Removal of Micropollutants from Wastewater

A. Fatima[a], A.P. Drdanová[b], F. Zažímal[a], J. Ryba[c], T. Mackuľak[b], A. V. Staňová [d,e], T. Homola*[a,b]

[a]Department of Plasma Physics and Technology, Masaryk University Brno, Czech Republic
[b]Department of Environmental Engineering, Slovak University of Technology, Bratislava, Slovakia
[c]Department of Polymer Processing, Slovak University of Technology, Bratislava, Slovakia
[d]South Bohemian Research Center of Aquaculture and Biodiversity of Hydrogenases, University of South Bohemia, České Budejovice, Czech Republic
[e]Department of Analytical Chemistry, Comenius University, Bratislava, Slovakia
(*554665@mail.muni.cz)

The advancement of human civilization has accelerated a significant water crisis posing serious risks to aquatic ecosystems and human health. Pharmaceutical waste, particularly antibiotics and anti-inflammatory medications, has emerged as a major contaminant. Graphitic carbon nitride (g-C_3N_4) has gained a lot of attention as photocatalytic agent for degradation of pollutants in wastewater as it has non-toxic nature, low cost, environment friendly precursors and visible range (2.7 eV) photocatalysis.

The aim of this study is to modify photocatalytically active PA6 membranes/fabrics by using plasma treatment with graphitic carbon nitride (g-C_3N_4) to enhance their performance in the removal and degradation of micropollutants. We employed atmospheric pressure plasma (diffuse coplanar surface barrier discharge) for modification of the PA6 nanofibers and g-C_3N_4 flakes. The fabrics were treated under various conditions, including distance, duration, and power, using plasma in ambient air, oxygen, and nitrogen environments, and their efficiency in removing selected micropollutants was evaluated. Surface sensitive techniques, i.e., XPS and BET are used to study the functionalization by plasma. Degradation efficiency was studied by spectrophotometer, HPLC and LC-MS. The most effectively modified fabrics were tested for their performance in treating real wastewater effluent.

Photocatalytically Active Bio-Inspired Fabrics for the Removal of Pharmaceutical Micropollutants in Wastewater

A.P. Drdanová[1], A. Fatima[2], F. Zažímal[2], J. Ryba[3], T. Mackuľak[1],
A. V. Staňová [3,5], T. Homola*[1,2]
[1]Department of Environmental Engineering, Slovak University of Technology, Bratislava, Slovakia
[2]Department of Plasma Physics and Technology, Masaryk University, Brno, Czech Republic
[3]Department of Polymer Processing, Slovak University of Technology, Bratislava, Slovakia
[4]South Bohemian Research Center of Aquaculture and Biodiversity of Hydrogenases, University of South Bohemia in České Budejovice, Czech Republic
[5]Department of Analytical Chemistry, Comenius University, Bratislava, Slovakia
tomas.homola@mail.muni.cz

The rapid growth of the global population and continuous advancements in human civilization have accelerated a significant water crisis, if discharged into natural water bodies without adequate treatment posing serious risks to aquatic ecosystems and human health. Pharmaceutical waste, particularly antibiotics and anti-inflammatory medications, has emerged as a major contributor to this contamination. Graphitic carbon nitride (g-C_3N_4) has gained considerable attention in recent years due to its low production cost, non-toxic nature, and stability under high temperatures.

Its bandgap of 2.7 eV (corresponding to wavelengths around 460–470 nm) allows for efficient harnessing of visible light, making it particularly effective in the degradation of organic pollutants in wastewater. Its efficiency is limited by poor adhesion to substrates and instability when exposed to water streams, leading to delamination and release into the water. To address these challenges, our research focuses on developing bio-inspired, photocatalytically active fabrics that mimic the structure of spider webs, incorporating g-C_3N_4 as the embedded photocatalytic material.

These fabrics, constructed from synthetic polymers fabricated by electrospinning, offer enhanced mechanical stability while retaining the photocatalytic properties of g-C_3N_4. In this study, comprehensive characterization techniques, SEM/EDX, XPS, BET surface area analysis, were employed to analyse the structure, composition, and properties of the developed fabrics. The photocatalytic activity was evaluated under various conditions, with the degradation process analysed using HPLC, EPR and LC-MS. Additionally, the performance of the fabrics was tested in real wastewater effluents to assess their effectiveness in complex environmental matrices.

Innovative Visible-Light-Responsive N-TiO_2 Photocatalyst/Fishery Waste Derived-Chitosan Composite with 3D Cartographic Insights into Microbial Cells Disinfection Mechanism

Ying-Chen Chen[1], Chih-Huang Weng[2], Shang-Ming Huang[3], Girma Sisay Wolde[4], Jing-Hua Tzeng[4, 5], Jenn-Wen Huang[6], Chanat Chokejaroenrat[7], Yao-Tung Lin[1, 4, *]

[1] Doctoral Program in Plant Health Care, National Chung Hsing University, Taiwan.
[2] Department of Civil Engineering, I-Shou University, Taiwan.
[3] Department of Nutrition, China Medical University, Taiwan.
[4] Department of Soil and Environmental Sciences, National Chung Hsing University, Taiwan.
[5]Department of Civil and Environmental Engineering, University of Delaware, USA.
[6] Department of Plant Pathology, National Chung Hsing University, Taiwan.
[7] Department of Environmental Technology and Management, Kasetsart University, Thailand

(*Corresponding author: yaotung@nchu.edu.tw)

The development of innovative packaging films has attracted increasing attention due to severe environmental pollution caused by petrochemical-based polymers and food safety concerns. For the first time, this study characterized a novel composite, including shrimp shell chitosan (CTS) and visible-light-responsive nitrogen-doped titanium dioxide (N-TiO_2), transmission X-ray microscopy (TXM), full-field soft X-ray tomography (SXT), atomic force microscopy (AFM), transmission electron microscope (TEM), and scanning electron microscopy (SEM) were first applied to explore the disinfection mechanism of Gram-positive bacteria (*S. aureus*) and Gram-negative bacteria (*E. coli*). N-TiO_2 is an outstanding photocatalyst due to its photo-disinfection activity, high chemical/physical stability, cost efficiency, and being environmentally friendly. Antibacterial experiment results indicated that 99.999% disinfection efficiency for *E. coli* and *S. aureus* was achieved using CTS-N-TiO_2 under visible light irradiation for 6 hours; 99% disinfection efficiency was achieved even without the light source. Kinetic model (Light-Responsive Modified Hom model) accounting for multiple key parameters, including k_1, k_2, k_3, and α, the light intensity can successfully describe the disinfection process. Furthermore, SEM and TXM showed the 2D and 3D surface morphology alterations of microbial cells. The destruction of the outer cellular caused leakage of cellular K^+ ultimately bringing about a severe decrease in cell survival rate. AFM and SXT characterized the decrease of cell height and intracellular organelles' shrinkage of microorganisms. Accordingly, TXM, SXT, AFM, and SEM techniques provided useful information for a clearer understanding of the damage caused by foodborne microorganism cells. Findings clearly demonstrated that the development of the novel CTS-N-TiO_2 photocatalyst alleviates the waste problems and can be used as an environmentally friendly photocatalyst.

Keywords: Visible-light-responsive photocatalysis; N-TiO_2; Shrimp shell; Chitosan; Antimicrobial activity

Testing the Antimicrobial Activity of Photocatalytic Surfaces via the Resazurin Assay

M. Kralova*, M. Veselá, M. Veselý, P. Dzik
Faculty of Chemistry, Brno University of Technology, Brno, Czech Republic
(*kralova@fch.vut.cz)

The antimicrobial activity of the photocatalytic active films was studied applying a resazurin assay [1]. Different types of microorganism were used as model organisms. The inoculum of microorganism with concentration of 4.8×10^6 CFU/mL was applied to hydrogel carriers, and these were consequently placed on the photocatalytic surfaces. The part of the samples was kept in the dark and the part was illuminated (3 mW/cm^2). After 4 hours, carriers were transferred to vials, resazurin was added and the vials were illuminated with a 530 nm wavelength radiation source. Under this green light, an increase in fluorescence due to resorufin production can be observed. The fluorescence intensity was recorded by taking a photograph every two minutes for a total of 800 minutes. The photographic record was then converted to video using the software program ImageJ. The time to reach maximum fluorescence was also evaluated using this program. This time correlates with the number of viable cells.

During the evaluation, the actual initial concentration (determined from fluorescence maxima) is always determined and compared with the theoretically calculated concentration. Next, the average log CFU/ml is determined for the photocatalytic surface in the light (C_L) and dark (C_D) and for the control (B_L and B_D). From these values, the final ΔR value is finally calculated:

$$\Delta R = R_L - log(B_D/C_D) = log(B_L/C_L) - log(B_D/C_D)$$

The applicability of the resazurin method was investigated on different species of microorganisms.

References:

[1] E. Travnickova, P. Mikula, J. Oprsal, M. Bohacova, L. Kubac, D. Kimmer, J. Soukupova, M. Bittner, Resazurin assay for assessment of antimicrobial properties of electrospun nanofiber filtration membranes, Amb Express, 9 (2019).

[2] M. Králová M. Králová, S. Patakyová, M. Veselá, M. Baudys, J. Viktorová, J. Krýsa, M. Veselý, P. Dzik, Resazurin assay as a suitable method for testing the antimicrobial activity of photocatalytic surfaces, Journal of Photochemistry and Photobiology A: Chemistry, Volume 455, 2024, 115769.

SESSION IV

Nanoarchitecture design of photocatalysts: Enhancement of photocatalytic performance and mechanism clarification

Ewa Kowalska
Jagiellonian University, Krakow, Poland
(*ewa.k.kowalska@uj.edu.pl; kowalska@cat.hokudai.ac.jp*)

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, has controlled 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.

References:

[1] Wei Z., Janczarek M., Zheng S., Wang K. & Kowalska E. (2020). *Catalysts*, 10, 1070.
[2] Kowalska E., Abe R. & Ohtani B. (2009). *Chem. Commun*., 2, 241.
[3] Wei Z., Rosa L., Wang K., Endo M., Juodkazis S., Ohtani B. & Kowalska E. (2017). *Appl. Catal. B-Environ*., 206, 393.
[4] Wei Z., Endo M., Wang K., Charbit E., Markowska-Szczupak A., Ohtani B. & Kowalska E. (2017). *Chem. Eng. J*. 318, 121.
[5] Wei Z., Janczarek M., Endo M., Balčytis A., Nitta A., Mendez Medrano M. G., Colbeau-Justin C., Juodkazis S., Ohtani B. & Kowalska E. (2018). *Appl. Catal. B-Environ*. 237, 574.
[6] Janczarek M., Wei Z., Mogan T. R., Wang L., Wang K., Nitta A., Ohtani B. & Kowalska E. (2021). *Symmetry* 13, 1682.
[7] Wei Z., Wu L., Yue X., Mu H., Li Z., Chang Y., Janczarek M., Juodkazis S. & Kowalska E. (2024). *Appl. Catal. B-Environ*. 345, 123654.

Acknowledgements:
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 (2023/51/B/ST4/01935).

Hydrodynamic Cavitation as a Novel Approach for Water and Wastewater Treatment

Parag R. Gogate
Chemical Engineering Department,
Institute of Chemical Technology, Matunga, India
E-mail: pr.gogate@ictmumbai.edu.in

Cavitation can be in general defined as generation, growth and subsequent collapse of the cavities releasing large quantum of energy locally with overall conditions remaining as ambient. The spectacular effects of cavitation viz. generation of highly reactive free radicals, local hotspots and liquid circulation associated by intense turbulence make cavitation a lucrative technique for water disinfection and wastewater treatment. The present work will initially highlight the different aspects of hydrodynamic cavitation reactors including mechanism of generation, reactor designs and optimum operating parameters with a special focus on water and wastewater treatment.

Experimental case studies based on the research work at Institute of Chemical Technology will also be presented. It has been conclusively shown that the pollutants consisting of various organic compounds such as dyes, pesticides and insecticides can be effectively degraded by hydrodynamic cavitation based treatment schemes. The effects such as molecular break down and its possible rearrangement (physicochemical effects) to improve the bio-digestibility index combined with partial COD reduction will also be described.

The successful application of hydrodynamic cavitation in a supplementary role, along with other advanced oxidation processes, including the use of other oxidizing agents such as H_2O_2, and O_3 will be described for application of microbial disinfection and industrial wastewater treatment, indicating the possible reasons and the range of synergy. The observed process intensification and the synergy will be explained on the basis of the role of inter-phase mass transfer enhancement, increase in the interfacial area, role of nucleation at the inter-phase boundary and the role of hydrodynamic cavitation in facilitating the same. A technology actually being implemented at commercial scale, which is based on the principle of combining the individual effects of Ozone, Hydrodynamic Cavitation, Acoustic Cavitation, and Electro-Chemical Oxidation to achieve synergistic effects, will also be highlighted in terms of basic design and case studies of applications.

Overall, it appears that the use of hydrodynamic cavitation result into a significant increase in the rates of degradation and also increases the scope of applicability of these techniques to more and more complex effluents containing a variety of pollutants. Proper optimization of the operating parameters should result in a substantial savings in the treatment costs for a cleaner environment which is indeed what is required in the current scenario.

Computational and Simulation Tools as Design Aids for Combined Air Purification Technologies

S. Denys*, D. Baetens, K. Schoofs, M. Demuynck, A. Alvarado and M. Ramteke
Antwerp engineering, photoelectrochemistry and sensing (A-PECS), University of Antwerp, Belgium
(*siegfried.denys@uantwerpen.be*)

In the pursuit of a healthier environment, the combination of multiple air purification technologies has emerged as a transformative strategy. Merging diverse purification techniques such as filtration, adsorption, electrostatic precipitation and photocatalysis, these systems offer enhanced performance and versatility in tackling complex air quality challenges[1].

This lecture highlights the power of simulation toolsnand computational modeling in the design and optimization of these combined systems. Using advanced tools like computational fluid dynamics (CFD), multiphysics, and system-level simulators such as Matlab Simulink, we demonstrate how these technologies enable the fine-tuning of system layouts, material properties, and operational settings to maximize efficiency while minimizing energy use and costs.
The discussion explores the interactions and synergies within key processes, including airflow dynamics, adsorption-desorption cycles, light distribution, and catalytic reactions [2,3,4]. The emphasis will be on light modelling and estimation of intrinsic kinetic PCO parameters which are fundamental properties of a chemical reaction that remain consistent regardless of external conditions or the physical state of the reactants and products. The succesful use of computational modelling will be discussed on both the fundamental level (submodels for the phenomena involved) and the design level (putting the models at work for designing and optimizing air purification technologies).

One of the most significant advantages of simulation and computational modeling is its ability to facilitate the exploration of innovative design concepts. Unlike traditional experimental approaches, simulation allows for rapid prototyping and testing of novel ideas under a wide range of conditions. This capability accelerates development timelines, reduces reliance on costly and time-intensive physical experiments, and identifies potential risks or limitations early in the design process. By simulating scenarios with varying pollutant loads, environmental conditions, and operational constraints, researchers can predict system performance with remarkable accuracy.

References:

[1] Donja Baetens, Kobe Schoofs, Nick Somers et al. A brief review on Multiphysics modelling of the various physical and chemical phenomena occurring in active photocatalytic oxidation reactors. Current Opinion in Green and Sustainable Chemistry **40**, 1-6 (2023).

[2] van Walsem J., Roegiers J., Modde B., et al. Integration of a photocatalytic multi-tube reactor for indoor air purification in HVAC systems: a feasibility study. Environmental Science and Pollution Research. **25**, 18015–26 (2018)

[3] Roegiers, J. & Denys, S. CFD-modelling of activated carbon fibers for indoor air purification. *Chem. Eng. J.* **365**, 80–87 (2019).

[4] Roegiers, J., Van Walsem, J. & Denys, S. CFD- and radiation field modeling of a gas phase photocatalytic multi-tube reactor. *Chem. Eng. J.* **338**, 287–299 (2018).

SESSION V

Photocatalysis Between Light and Shadow: How Misinterpretation of Data Hinders Progress

C. Guillard
University Lyon, University Claude Bernard, CNRS, IRCELYON, France
chantal.guillard@ireclyon.univ-lyon1.fr

In the 20th century, scientific production in photocatalysis experienced a surge, with over 15,000 articles published annually. This research covers various fields such as the environment (pollution control materials, air treatment, wastewater treatment) and energy (H2 production, CO2 reduction to methane and/or alkene, N2 reduction to NH3, biomass valorization). Most recent studies focus on (1) the development of new photocatalysts active under visible light, but also infrared (upconversion), and (2) CO2 reduction and H2 production. Some research even explores photocatalysis in the dark.

However, although these studies attract industrial interest and receive funding, many conclusions are sometimes unjustified. These overly confident claims would benefit from a more nuanced interpretation, as they limit the true advancement of progress in the field.

The presentation will begin with a reminder of the principle of photocatalysis and its limitations, followed by some examples of studies, including the results obtained and the proposed interpretations. This will be followed by questions and alternative interpretation suggestions. The possibility of transferring the process to industry for various applications will also be discussed, with a focus on the actual feasibility.

The impact of shell thickness in Au@TiO_2 core-shell nanoparticles on balancing stability and plasmonic field enhancement

Rajeshreddy Ninakanti[1,2,3] & Sammy W. Verbruggen[1,2*]
[1]Antwerp engineering, photoelectrochemistry and sensing (A-PECS),
University of Antwerp, Belgium
[2] NANOlight Center of Excellence, University of Antwerp, Belgium
[3] EMAT, University of Antwerp, Belgium
*Sammy.Verbruggen@uantwerpen.be

Fabrication of plasmonic core-shell nanostructures can have a positive impact on the efficiency of a photocatalytic reaction. The shell ensures improved stability of the nanoparticle cores, while at the same time light absorption is extended, and electron-hole pair separation occurs more effectively. However, successful synthesis of metal@TiO_2 core-shell nanoparticles with nanometer control over the shell thickness remains challenging. In addition, the exact impact of the shell thickness on the resulting photocatalytic efficiency, is poorly understood. In the present study, a method is presented for the accurate and reproducible synthesis of Au@TiO_2 core-shell nanoparticles with ultra-thin shells that can be tuned in the range of 2 to 12 nm.

The protocol relies on the controlled slow hydrolysis of a bulky titanium precursor. Based on a combined rigorous experimental and modeling approach, we show that extremely thin shells in the order of 2 nm are not capable of preventing sintering of the metal cores upon annealing, which leads to a loss of plasmonic properties and photocatalytic activity. After reaching an optimum shell thickness of 4 nm, a further increase in shell thickness again reduces the plasmonic properties by a weakened plasmonic coupling. This trend is experimentally demonstrated using photocatalytic hydrogen evolution experiments, and stearic acid degradation tests. With this study we prove and emphasize the crucial importance of carefully controlling the shell thickness in plasmonic core-shell structures, so their maximum application potential may be unlocked.

References:

R. Ninakanti, R. Borah, T. Craig, R.-G. Ciocarlan, P. Cool, S. Bals, S.W. Verbruggen (**2024**), Au@TiO2 core-shell nanoparticles with nanometer-controlled shell thickness for balancing stability and field enhancement in plasmon enhanced photocatalysis, *ACS Nano* (doi.org/10.1021/acsnano.4c09944)

Progress of Perovskite Solar Cells on Multiporous-Layered Electrode for Cost-Effective Hydrogen Energy Source

Seigo Ito
Department of Materials and Synchrotron Radiation Engineering, Graduate School of Engineering, University of Hyogo, Japan

Organic-inorganic metal halide perovskite solar cells (PSCs) were developed by Prof. T. Miyasaka's group in 2009, and the PCE has rapidly increased by over 26.6%, now. In order to fabricate cost-effective and high-stable PSCs for the commercialization, our group has focused on the fabrication of multi-porous-layered-electrode PSCs (MPLE-PSCs). All layers in MPLE-PSCs are porous materials and consist of an electron transport layer (e.g., mesoporous TiO_2), an insulating layer (e.g., mesoporous ZrO_2 or Al_2O_3), and a carbon back contact electrode.

All these porous scaffold layers are fabricated by the screen-printing method and sintered at 400 to 500 °C. The perovskite precursor solution is dropped cast onto the porous layered electrodes and permeated. Then, the porous layer is filled with perovskite crystals by heating and drying process to complete the device. MPLE-PSCs have been proven by many researchers to have exceptional stability due to the high moisture resistance provided by the thick carbon electrode (~10 μm). Furthermore, the stability of MPLE-PSC has been shown to be equivalent to a 20-year guarantee in outdoor use (experimental acceleration test over 3,000 h in damp-heat tests (85 °C and 85% RH.) in accordance with IEC 61215:2021), emphasizing that this carbon-based device is a key technology for the commercialization of PSCs. In this conference, the latest results of our group will be introduced.

Surface Nano-Engineering Towards Enhanced Photocatalytic Processes

Stěpán Kment[1,2]
[1]Regional Centre of Advanced Technologies and Materials, Czech Advanced Technology and Research Institute, Palacký University, Czech Republic
[2]Nanotechnology Centre, CEET, VSB-Technical University of Ostrava, Czech Republic

Photocatalysis based on semiconductor materials, particularly metal oxides such as TiO_2, is a promising approach for sustainable energy conversion and environmental remediation. However, improving efficiency in key processes such as solar-driven hydrogen production via water splitting, selective H_2O_2 formation, and CO_2 reduction to hydrocarbons requires precise control over surface properties. Surface engineering strategies, including defect engineering and co-catalyst decoration, play a crucial role in tuning electronic structure, charge carrier dynamics, and reaction selectivity.

A key aspect of defect engineering involves the introduction of oxygen vacancies, which can modify band structures, enhance charge separation, and introduce surface states that facilitate catalytic reactions. In parallel, the integration of metal co-catalysts significantly influences reaction kinetics and selectivity. Among emerging strategies, single-atom co-catalysts (SACs) have attracted increasing attention due to their unique ability to maximize metal utilization, minimize aggregation, and provide well-defined active sites with tunable electronic properties.

SACs are typically synthesized through methods such as atomic layer deposition, wet impregnation, or defect-assisted anchoring, where the strong metal-support interaction plays a crucial role in stabilizing single atoms against migration and agglomeration. Despite their potential, challenges remain in precisely controlling their coordination environment, stability under reaction conditions, and understanding their dynamic behavior at the atomic scale. Advances in operando spectroscopy and theoretical modeling provide new insights into the electronic and catalytic properties of SACs, guiding the design of highly active and selective photocatalysts.

By integrating defect engineering and SAC strategies, significant progress is being made in overcoming efficiency limitations in photocatalytic hydrogen production, oxygen activation for H_2O_2 synthesis, and selective CO_2 reduction to hydrocarbons. These approaches open new avenues for enhancing photocatalytic processes, bringing them closer to practical applications in renewable energy and green chemistry.

Advanced Oxidation Processes for the Degradation and Detoxification of Cyanotoxins

Zeynep Eren
Ataturk University, Engineering Faculty, Environmental Engineering Department, Erzurum, Türkiye
*Email: zeren@atauni.edu.tr

The occurrence of toxic cyanobacteria in freshwater has been increasing in both frequency and distribution in recent years due to increasing water pollution and global temperatures increase. The harmful algal blooms (HAB) in surface waters and reservoirs are one of the most important problems encountered in the supply of safe drinking water. Cyanobacteria cause significant costs in drinking water treatment plants (DWTPs) because the various metabolites, toxins and taste and odor compounds they produce cause significant water quality problems. Repeated sublethal or low-level exposure to cyanotoxins potentially causes gastrointestinal, neurological and liver disorders, posing a long-term chronic human health hazard [1]. Therefore, the protection of drinking water resources is becoming increasingly important. A multi-barrier approach consisting of prevention, source control, treatment optimization and monitoring is required to reduce the risk of toxic cyanobacterial growth in drinking water [2]. But it is stated that traditional processes disrupt the cell structure causing cell lysis and forming the presence of cyanobacterial toxins. However, later studies focused on Advanced Oxidation Processes (AOPs) of cyanotoxins DWTPs [3]. Therefore, this study focuses on the treatment of the microcystins (MCs) as most common detected group of cyanotoxins with ultrasonic oxidation and photocatalytic oxidation as well as their toxicity reduction.

Keywords*:* Ultrasound, Photocatalytic oxidation, Cyanotoxins, Microcystins

References:

[1]. Apeldoorn, M. E., van Egmond, H. P., Speijers, G. J. A. and Bakker, G. J. I. 2007. “Toxins of cyanobacteria”, Molecular Nutrition & Food Research 51, 7–60.
[2]. He, X., Liu, Y. L., Conklin, A., Westrick, J., Weavers, L. K., Dionysiou, D. D., ... Walker, H. W. 2016. “Toxic cyanobacteria and drinking water: Impacts, detection, and treatment”, Harmful algae, 54, 174-193.
[3]. Song, W., Teshiba, T., Rein, K., & O'Shea, K. E. 2005. “Ultrasonically induced degradation and detoxification of microcystin-LR (cyanobacterial toxin)”, Environmental science & technology, 39(16), 6300-6305.

Acknowledgements and Funding:

This study was conducted with the grant from Tubitak 119Y414 and 123Y445 projects.

SESSION VI

UV-C/H2O2 for Removal of Organic Pollutants – from Laboratory to Practice

Pavel Krystyník
Faculty of Environment, Jan Evangelista Purkyně University, Ustí nad Labem, Czech Republic
pavel.krystynik@ujep.cz

The lecture explores the development and optimization of a system based on the direct photolysis of hydrogen peroxide using UV radiation to generate hydroxyl radicals. This highly efficient technology offers significant potential for removing organic contaminants from polluted water, particularly in cases where conventional treatment methods are ineffective (e.g., phenolic substances and other aromatic hydrocarbons, chlorinated hydrocarbons or nitrogenous aromatic compounds). The technology is specifically designed for addressing industrial pollution in groundwater and/or process water. The presentation will follow path of the developed technology from initial laboratory research to its practical implementation in real-world application.

Ultraviolet Ultrasound and Solar Light Activated Persulfate Oxidation for the Removal of Endocrine Disruptors from Water

Slyvia Kpange, Olanireti Oni, Şifa Doğan, Saltuk Pirgalıoğlu
Cyprus International University, Nicosia, North Cyprus

This study focuses on laboratory scale and outdoor applications of selected advanced oxidation processes (AOPs – Figure 1) for the removal of acetaminophen from water solutions. Acetaminophen removal (measured with Shimadzu High Performance Liquid Chromatography) and mineralization (measured with Shimadzu Total Organic Carbon Analyzer) were the two key parameters to evaluate the performances of the selected AOPs. UV and Solar radiation activated persulfate process showed complete removal and high mineralization percentages after 90 minutes indicating to be a promising technique for the post-treatment application however, ultrasonic radiation has the limited potential to mineralize acetaminophen.

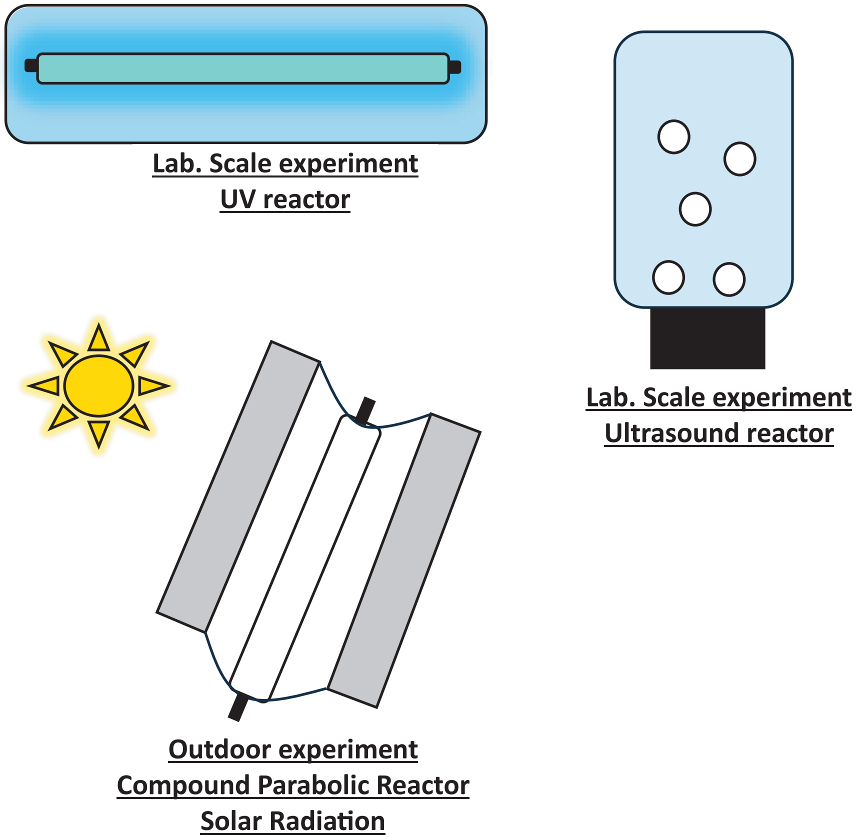


Figure 1. Selected AOPs for the removal of acetaminophen from water

Full Scale Project with a Combined In Situ Surfactant Enhanced Flushing and Chemical Oxidation Technology for the Remediation of Organic Compounds

Guido Piepoli
A.S.T.C. Remediation srl, Italy
email contact: guidopiepoli@astc.it

Technology definition

In order to increase the efficiency in the in situ tratments, it is necessary to combine different processes, to reach the remedial target.
According to the Italian Environmental Law (D.Lgs. 152/06, Art. 243) it's possible to inject reagents and recirculate them, as long as the contamination is kept under control and no further pollution is generated through this process.
What we've developped is a combined use of physical and chemical remediation approaches:

- ISSEF: In Situ Surfactant Enhanced Flushing Technology,
- ISCO: In Situ Chemical Oxidation Technology,

to increase soil and groundwater treatment efficiency, save costs, and meet an inflexible remedial goal.

A pre-treatment takes the recalcitrant compounds in account: hydrophobic contaminants are solubilized in water through the use of a specific surfactant. By definition, oil and water phases are immiscible. The role of the amphiphile is to reduce the miscibility gap, until the three components of a surfactant-oil-water (SOW) system are solubilized into a so-called microemulsion. This microemulsion can now easily be extracted. The surfactant we apply has been developed for the enhanced oil recovery and is readily biodegradable; >60%; 28 d; OECD Test Guideline 301B. The residual organic mass might then oxidized.

Environmental investigations and tests

We first defined the contamination distribution through a MIP site characterization. Afterwards we designed and performed the full-scale project going through a pilot test.
Laboratory and field tests carried out, showed the correspondence between what estimated at the design stage and what achieved in terms of results in the application phase.

In the field test we applied a hydrogen peroxide sodium persulfate technology. Although we've reached the designed target level but not the law limit, it was clear, that neither a single chemical compound, nor a single technology was sufficient to obtain the target results. The most critical topic was to get contaminant mass into the same phase as the reagents were and then the reaction had to be performed rapidly, in order to reduce the rebound effect. Therefore, to increase desorption, an ISSEF pretreatment was carried out.

Full-scale application

Through an automatic self-developped plant, we prepare a specific designed surfactant solution. Then, through a pressurization section the chemicals are delivered to several remote stations. A distribution system inject the surfactant and simustaniously extract the

contaminated water to create a local circulation. The polluted solutions are sent to the treatment plant to separate contaminants and ricirculate water back to the mixing station.
In the presented project, the contaminated area (~1˙750m^2÷12˙500m^3) was treated through a total of 78 injection and 24 extraction/monitoring wells. The contaminant compounds to treat, hydrocarbons, had a concentration up to 7˙600$^{mg}/_{kg}$ in soil.

The site was divided into two subareas and the treatment was performed in batch starting from the ISSEF technology. The whole treatment last 18 weeks and we injected roughly 700 m^3 of a surfactant solution and 200 m^3 of sodium persulfate activated sodium hydroxide.

This project was certified by the Local Authorities for the accomplishment of the reclamation targets and site closure.

Visible light photo-degradation of antibiotics with graphitic carbon nitride thin films: Pathways and toxicity of byproducts

D. Schimon[1,4*], P. Klusoň[1], P. Dzik[2], T. Homola[3], P. Stavárek[1]
[1] Institute of Chemical Process Fundamentals v.v.i., Czech Academy of Sciences,
Czech Republic
[2] Institute of Physical and Applied Chemistry, Faculty of Chemistry, Brno University of
Technology, Czech Republic
[3] R&D Centre for Plasma and Nanotechnology Surface Modifications, Faculty of Science,
Masaryk University, Czech Republic
[4] Faculty of Chemical Engineering, University of Chemistry and Technology Prague,
Czech Republic
(*schimon@icpf.cas.cz)

Graphitic carbon nitride (g-C_3N_4) is a metal-free, biodegradable photocatalyst exhibiting advantageous physical and electrochemical properties. It has been extensively employed in photocatalysis, electrocatalysis, heterogeneous catalysis, pollutant degradation, and water splitting. Its reduced band gap (2.7 eV) relative to TiO_2 (3.2 eV) facilitates enhanced visible-light absorption.

In this study, g-C_3N_4 was synthesized via calcination of a supramolecular complex comprising melamine and cyanuric acid at 550°C under a nitrogen atmosphere, yielding an enhanced photocatalyst [1].Thin films of g-C_3N_4 were subsequently fabricated using ball-milled g-C_3N_4 and a polysiloxane binder. These films, with an average thickness of 27 µm, were subjected to plasma treatment to improve surface hydrophilicity. The photocatalytic efficacy of the films was assessed in a photomicroreactor (PMR) with a slit geometry and compared against a batch photoreactor (BPR) operating with a photocatalyst slurry. Rhodamine B (RhB) served as a reference dye, while tetracycline (TC) and trimethoprim (TMP) were examined as representative antibiotic pollutants.

The PMR operated as a differential reactor, with minimal conversion occurring during a single pass. A reaction volume of 432 µl was continuously irradiated, while a 25 ml reaction mixture circulated at a flow rate of 63 ml/min. Conversely, in the BPR, the entire 25 ml volume was exposed to continuous irradiation. To facilitate a direct comparison, the effective irradiation time in the PMR was calculated by normalizing the total reaction time using the ratio of reaction mixture volume to PMR volume. Pollutant concentration variations over time were analyzed via HPLC-MS, assuming pseudofirst-order reaction kinetics. The data from both reactors were analyzed by evaluating the specific initial reaction rate r_0, determined using the following equation, where k represents the kinetic constant, c_0 is the initial pollutant concentration, and m_{cat} denotes the mass of the catalyst within the reaction volume.

$$r_0 = \frac{k \times c_0}{m_{cat}}$$

To ensure consistency in irradiation conditions across both reactors, identical frontal irradiated areas, light source distances, and other relevant parameters were maintained.

The specific initial reaction rates in the PMR and BPR were analyzed using the reaction rate enhancement factor, expressed as the ratio $r_{0,PMR}/r_{0,BPR}$. The most significant enhancement was observed for TMP degradation, with the PMR exhibiting a 25.4-fold increase compared to the BPR. Across all experiments, RhB, TC, and TMP achieved conversion efficiencies of at least 87% in both reactor configurations.

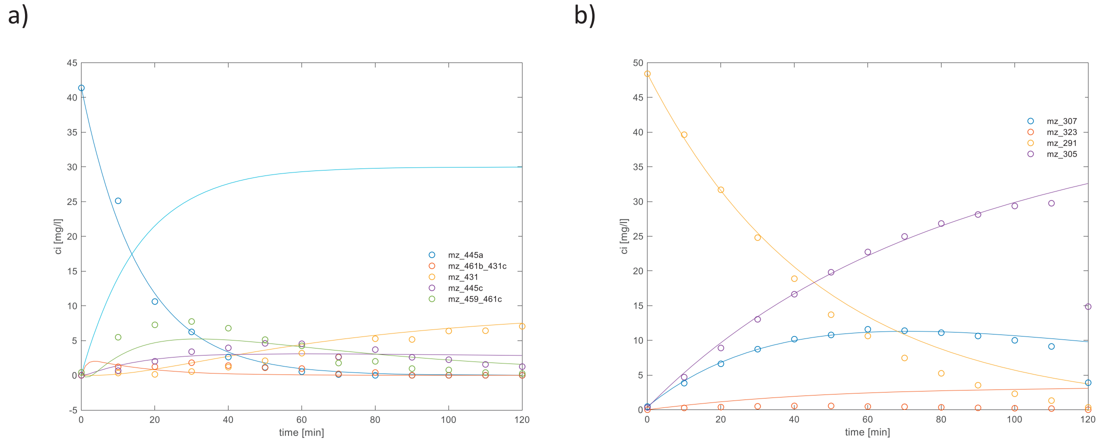


Figure 1: Experimental data depicting batch photodegradation of Tetracycline (a) and Trimethoprim (b), alongside kinetic model predictions. (Reaction components quantified via HPLC-MS).

HPLC-MS analysis identified intermediates generated during photodegradation. The findings were correlated with established degradation pathways [2-5], and a mathematical model was developed to describe the observed mechanisms, see Figure 1. The degradation pathways were proposed based on experimental conditions, and corresponding reaction rate constants were determined. The toxicity of photodegradation intermediates of TC and TMP was assessed.

Acknowledgments

Authors acknowledge Czech Science Foundation for financial support under grant no. 23-06843S

References:

[1] Dolai, S., et al., *Graphitic carbon nitride thin films for light-induced photocatalysis in a slit geometry microreactor.* Journal of Environmental Chemical Engineering, 2022. **10**(6): p. 108790.

[2] Li, R., et al., *Activation of peroxymonosulfate by Fe doped g-C3N4 /graphene under visible light irradiation for Trimethoprim degradation.* Journal of Hazardous Materials, 2020. **384**: p. 121435.

[3] Li, S. and J. Hu, *Photolytic and photocatalytic degradation of tetracycline: Effect of humic acid on degradation kinetics and mechanisms.* Journal of Hazardous Materials, 2016. **318**: p. 134-144.

[4] Sirtori, C., et al., *Effect of water-matrix composition on Trimethoprim solar photodegradation kinetics and pathways.* Water Research, 2010. **44**(9): p. 2735-2744.

[5] Shen, M., et al., *Activation of persulfate for tetracycline degradation using the catalyst regenerated from Fenton sludge containing heavy metal: Synergistic effect of Cu for catalysis.* Chemical Engineering Journal, 2020. **396**: p. 125238.

Preparation and Characterization of WO_3 Layers Fabricated by the Brick-and-Mortar Method

T. Blecha[1, *], M. Králová[1], P. Dzik[1], M. Veselý[1]
[1]Institute of Physical and Applied Chemistry, Faculty of Chemistry,
Brno University of Technology, Czech Republic
(**Tomas.Blecha1@vut.cz*)

With rapid population growth and industrialization, continuous consumption of fossil fuel reserves and environmental pollution are urgent issues that need to be addressed. In a similar vein, organic pollutants, such as pharmaceuticals and personal care products, are major water pollutants due to their limited biodegradability[1]. Thus, development of green energy production and environmental rehabilitation is crucial. One of the most important sources of renewable energy is sunlight, however its conversion and storage is difficult to achieve[2].

Heterogeneous photocatalysis based on semiconductors is a green method of converting solar energy into chemical energy. In a typical photocatalytic reaction, photocatalyst is activated by irradiation and subsequently generates electron-hole pairs. These pairs then can emulate redox reactions over the surface of photocatalyst and generate reactive oxygen species, which can decompose organic pollutants into less hazardous materials[3]. If the electric field is applied between the photocatalyst and a cathode, electrons and holes inside the photoanode are separated and the photoelectrochemical cell can thus allow the flow of electric current[4].

Tungsten oxide (WO_3) is a non-toxic semiconductor with excellent photocatalytic activity on visible light radiation. This is due to lower bandgap of under 3 eV, which allows WO_3 to efficiently use solar energy for photocatalytic reactions[3]. For our application, thin layer of photocatalyst is immobilized on transparent conductive oxide glass, such as fluorine-doped tin oxide (FTO) glass.

Semiconductor photocatalysts are synthesized in two different ways – disintegration of crude material by mechanical processing (top-down), or assembly of atoms and molecules to form nanoparticles (bottom-up). Combining these two methods creates dual-phase material, consisting of nanoparticles ("bricks") and amorphous matrix ("mortar"). The combination of these two different approaches allows better configuration of structure on micro to nano scale and elevates or creates new properties.

Such composite was prepared using ball-milled WO_3 nanoparticles and solution of amorphous WO_3 precursor. The prepared compositions with the addition of templating agent were deposited on FTO glass and annealed at high temperatures. Using different analytical methods, the influence of the milled nanoparticles size and the amount of amorphous matrix in composition on physicochemical properties of the prepared photocatalysts was studied. The results show that physical properties, and importantly photocatalytic activity, of the prepared WO_3 thin films were heavily influenced by the two variables. Layers with larger nanoparticles and smaller amount of binder were most efficient at generating high photocurrent.

References:

[1] M. G. Peleyeju, E. L. Viljoen, *Journal of Water Process Engineering* 40 (2021) 101930.
[2] J. Y. Zheng et al., *Applied Catalysis B: Environmental* 233 (2018) 88–98.
[3] V. Dutta et al., *Journal of Environmental Chemical Engineering* 9 (2021) 105018.

[4] M. B. Costa et al., *Journal of Energy Chemistry* 73 (2022) 88–113.

Coprecipitation-Hydrothermal Synthesis of Conductive Sb-doped SnO_2 for Carbon-free Catalyst Support of PEMFC

T. Fukuda[1], Y. Yoshiyama[1], N. Fukumuro[1], S. Ito[1]*

[1]Department of Materials and Synchrotron Radiation Engineering, Graduate School of
Engineering, University of Hyogo, Hyogo, JAPAN
*(*itou@eng.u-hyogo.ac.jp)*

Proton-exchanged-membrane fuel cell (PEMFC) is an important energy device for the realization of a hydrogen society. However, a longer running lifetime is essential for the further application of PEMFCs. Currently, platinum supported on carbon (Pt/C) is the most mainstream cathode catalyst. But it has durability issues due to carbon degradation during high potential sweeps. As an alternative material to carbon, tin oxide (SnO_2) is attracting attention due to its electrical conductivity and chemical stability. It has already been reported that Pt/SnO_2 catalysts using SnO_2 doped with antimony (Sb) and they exhibit high durability [1, 2]. For the practical use of Pt catalysts using Sb-SnO_2 (Pt/Sb-SnO_2) and their large-scale diffusion, it is essential to improve the catalytic activity of Pt/Sb-SnO_2, further. Since the catalytic activity of Pt/Sb-SnO_2 depends on the crystallinity, morphology, and conductivity of Sb-SnO_2, it is important to study and optimize the Sb-SnO_2 synthesis method. In this study, we focused on the coprecipitation method and the hydrothermal method to synthesize the Sb-SnO_2 nanoparticles, which have been used as industrial synthesis methods and are also used as laboratory-scale methods. Now, we developed a new synthesis method (coprecipitation-hydrothermal hybrid synthesis), and evaluated the prepared Sb-SnO_2 and Pt/Sb-SnO_2.

In the experimental methods, tin fluoride (SnF_2) and antimony chloride ($SbCl_3$) mixed in distilled water. After adding tetramethylammonium (TMAH), the solution stirred for 3 days. The solution was transferred to a Teflon internal-vessel and stainless-steel-out jacket autoclave and placed in an electric furnace at 240℃. The precipitate was dispersed in methanol and centrifuged 3 times. Finally, the solution was dried on a hot plate at 60℃ to be named "coprecipitation-hydrothermal Sb-SnO_2". Pt/Sb-SnO_2 was prepared using the polyol method. The prepared coprecipitation-hydrothermal Sb-SnO_2 powder was mixed and dispersed in a mixed solvent of ethylene glycol and water, then platinum chloride hexahydrate was added and stirred overnight. The solution was then heated at 120°C for 2 hours to produce the platinum nanoparticles on the Sb-SnO_2 surface. Catalytic performance was evaluated by electrochemical measurements (cyclic voltammetry (CV) and linear sweep voltammetry (LSV)) using a three-electrode cell. The material characterization was also conducted for Sb-SnO_2 and Pt/Sb-SnO_2, and the factors of catalytic performance enhancement were investigated.

The performance of using coprecipitation-hydrothermal Sb-SnO_2 was compared with that of Sb-SnO_2 using the simple coprecipitation (coprecipitation Sb-SnO_2) and hydrothermal methods (hydrothermal Sb-SnO_2). X-ray diffraction (XRD) showed that highly crystalline Sb-SnO_2 nanoparticles were synthesized in coprecipitation-hydrothermal Sb-SnO_2. On the other hand, impurities were mixed in hydrothermal Sb-SnO_2, and poorly crystalline Sb-SnO_2 was synthesized in coprecipitation Sb-SnO_2. TEM image of coprecipitation-hydrothermal Sb-SnO_2 showed angular nanoparticles with a diameter of about 10 nm. The electrical conductivity of Sb-SnO_2 and the catalytic performance of Pt/Sb-SnO_2 were compared. As a result, coprecipitation-hydrothermal Sb-SnO_2 showed the best results in both cases. This is due to the appropriate doping of Sb by coprecipitation and the improvement of crystallinity by hydrothermal treatment.

References:

[1] K.Kakinuma, *et al., Electrochim. Acta.,* **2013** 110, 316-324.
[2] T. Fukuda, S. Ito, *et al., Crystal,* **2024**, 14, 462.

Photocatalytic Efficiency of Thermally Treated Muscovites

Patrik Kopčan [1, 2]*, Miroslava Filip Edelmannová [1], Marta Valášková [1], Bartosz Romuald Zawadzki [1], Kamila Kočí [1, 3]
[1] Institute of Environmental Technology, CEET, VŠB-Technical University of Ostrava, Czech Republic
[2] Faculty of Materials Science and Technology, VŠB-Technical University of Ostrava, Czech Republic
[3] Department of Physics and Materials Engineering, Faculty of Technology, Tomas Bata University, Czech Republic
(*patrik.kopcan@vsb.cz)

The global energy crisis and climate change necessitate a transition toward renewable energy sources. Fossil fuels, which currently dominate the energy market, are not only environmentally detrimental due to greenhouse gas emissions but are also depleting at an alarming rate. This depletion, coupled with geopolitical dependencies and fluctuating prices, underscores the urgency of developing sustainable energy alternatives. Hydrogen is an ideal candidate for energy storage and conversion, as it offers high energy density and generates only water upon combustion. However, conventional hydrogen production methods, such as steam methane reforming, contribute to carbon emissions, necessitating the development of eco-friendly alternatives. Photocatalytic methanol solution decomposition presents a viable approach to hydrogen production, leveraging light to drive the breakdown of methanol into hydrogen and carbon dioxide. Methanol serves as an efficient energy carrier due to its ease of storage, transport, and high hydrogen content. By integrating muscovite-based photocatalysts, the oxidation process can be enhanced, improving both hydrogen yield and reaction efficiency. Among various photocatalytic materials, muscovite, a naturally abundant phyllosilicate mineral, has gained attention due to its potential to support efficient hydrogen evolution reactions and good structural stability. Muscovite's natural abundance and cost-effectiveness make it a competitive material for scalable hydrogen production. We explored multiple different materials derived from naturally occurring muscovite from two locations – China, Czechia; and we let them undergo different thermal treatment. The changes in photocatalytic properties and the mechanism of photocatalysis of thermally treated muscovites have not been reported to date. Given its lamellar morphology and negative layer charge, muscovite powder was thermally treated at 500–700 °C and used as the photocatalytic matrix. Structural properties were analyzed using X-ray diffraction, while optical characteristics were examined via ultraviolet-visible diffuse reflection spectroscopy. The prepared materials were examined for hydrogen production activity from methanol-water mixture in the batch reactor with 8 W Hg lamp. Our investigation aimed to elucidate the intricate interplay between the synthesis process, stability of prepared materials and the quantity of hydrogen produced. This contribution highlights the potential of muscovite-based photocatalysts in addressing energy challenges while emphasizing the environmental and economic benefits of hydrogen as an energy carrier. By advancing research in this field, we can move closer to a cleaner, more sustainable future, reducing our reliance on fossil fuels and mitigating their adverse environmental impacts.

Acknowledgements: This work was financially supported by 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. The work was supported by Large Research Infrastructure ENREGAT (project No.LM2023056).

Multifunctional $Bi_xO_yI_z$: Integrating Photocatalysis and Cooling for Eco-friendly Building Solutions

Andrea Martínez-Topete[1,2], Eva Jimenez-Relinque[1], Frederic Dappozze[3], Christophe Gilbert[4], Chantal Guillard[3], Andrea Folli[5], Marta Castellote[1]
[1] Institute of Construction Science Eduardo Torroja, IETcc-CSIC, Madrid, Spain
[2] Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid (UPM), Madrid, Spain
[3] Université Claude Bernard Lyon 1, CNRS, Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), France
[4] Centre International de Recherche en Infectiologie (CIRI), INSERM U1111, ENS Lyon, CNRS, France
[5] Net Zero Innovation Institute, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Translational Research Hub, UK

Photocatalysis has become a promising technology for pollutant degradation. While many semiconductor materials require UV light for activation, the search for visible-light-active materials offers more practical and sustainable solutions. Additionally, passive cooling through materials with high NIR reflectance and emissivity is key for enhancing energy efficiency in buildings. This study explores the synthesis and performance of bismuth oxyiodides ($Bi_xO_yI_z$), investigating their dual functionality in photocatalytic and cooling applications for sustainable construction.

$Bi_xO_yI_z$ (BiOI, Bi_5O_7I, $Bi_4I_2O_5$) were synthesized employing much less energetically-demanding techniques, with co-precipitation identified as the most effective method. This process utilizes water as the solvent and operates under mild conditions, eliminating the need for elevated temperatures. This approach not only minimizes the environmental impact but also ensures the scalability and sustainability of the synthesis process. The electronic structure and morphology of the materials were found to be critical for achieving efficient photocatalytic activity; with careful control over these parameters, their performance under both UV and visible light was enhanced.

The photocatalytic tests conducted on various pollutants, including nitrogen oxides (NOx) in air, phenol in water, and *E. coli* bacteria inactivation, demonstrated the promising performance of the materials under visible light, being this a key advantage over conventional photocatalysts, which typically require UV light. The results showed that $Bi_xO_yI_z$ achieved up to 15% removal of NOx in a continuous flow system. In the case of phenol degradation, up to 85% reduction in the initial phenol concentration ($[\text{phenol}]_i = 20$ ppm) was observed and intermediate products were carefully analyzed to better understand the degradation mechanism. For *E. coli* inactivation, after 180 minutes of irradiation, more than 99% of the bacteria were inactivated, highlighting the material's excellent antibacterial properties.

Mechanistic studies of photocatalysis were conducted using Electron Paramagnetic Resonance (EPR), fluorescence probes, and scavenger experiments. These studies revealed interesting results, showing that the photocatalytic behavior of the $Bi_xO_yI_z$ catalysts synthesized on this work differs from that reported in the literature, offering unique insights into the reaction pathways involved in the degradation processes.

In addition to their photocatalytic properties, the synthesized materials were evaluated for cooling performance in powder, alkyd-resin, and paint forms. These materials exhibited multifunctional capabilities, showing promising cooling effects where high NIR reflectance and emissivity were observed. On the inner surface the $Bi_xO_yI_z$ coated steel plates exhibited a temperature reduction of 10ºC compared to the uncoated samples, demonstrating a significant cooling effect. This dual functionality—both photocatalysis and cooling—sets these materials apart from conventional photocatalysts and opens new possibilities for their use in sustainable construction, where they can contribute to both environmental pollution reduction and energy efficiency.

SESSION VII

A Review of Kinetic Models in Photocatalysis, Their Evaluation, Applicability and Inherent Limitations.

Claudio Minero , Fabrizio Sordello
University of Turin, Dept. of Chemistry, Italy

The mechanisms operating in photocatalysis are complex, starting from the reactivity of e_{CB} and h_{VB} with both RID and OX with indirect mechanisms (reactive site + substrate in solution), direct mechanisms (site complexed with substrate that acts as a trap for e_{CB} and h_{VB}). The structure or modification of the surface changes the relative role of both mechanisms. [1]. The two mechanisms can lead to different oxidation products. A typical case is glycerol. [2] Isotopic studies with labeled O_2 and H_2O have attempted to clarify the mechanism of oxygen incorporation. This complexity cannot be ignored in macroscopic kinetic models that have great importance not only in photocatalysis applications, but also in basic studies for a comparison of performances of various photocatalytic materials.

The first kinetic models in photocatalysis and their development will be briefly reviewed, along with a critical examination of the fundamental aspects introduced. A simple quadratic model (QM0, [3]) has proven to be highly effective in evaluating reaction rates both in solution and for gas/semiconductor systems. [ref] outperforming the Langmuir-Hinshelwood (LH)-based model, which lacks a chemically sustainable kinetic basis, but is still widely and erroneously used.

An alternative to the measurement of the RID degradation rate as a function of [RID] for the validation of a macrokinetic model is the measurement of [e_{CB}] as a function of [RID]. In fact, [e_{CB}] appears in all kinetic equations, starting from the recombination rate e_{CB} + h_{VB}. Photoelectrochemical measurements of [e_{CB}] were performed on various RID substrates as a function of [RID] (formic acid FORM at two different O_2 concentrations, methanol MeOH, glycerol GLY, phenol PhOH at three different O_2 concentrations, catechol CAT). For FORM, MeOH and GLY, [e_{CB}] increases as a function of [RID], while for PhOH and CAT it decreases. This behavior is similar to that observed on the rate evaluated by the rate of disappearance of RID. It is evident that the QM0 model is not generally applicable.

A possible kinetic model should consider direct and indirect pathways together with the balance of the surface sites and all possible recombination paths of e_{CB} and h_{VB}. This minimal model has to consider at least 16 parameters (7 for the semiconductor CAT, 4 for the oxidant B+CAT, 4 for the substrate A+CAT and 1 for A+B+CAT). The solution for [e_{CB}] (or h_{VB}) also under the steady state approximation can obviously be obtained only with numerical methods, it is complex and unreliable for a least squares fit on the experimental data. In an attempt to have an analytical equation (as a solution of a second order polynomial) we made a series expansion on [e_{CB}] and used the first (QM1) and second (QM2) order approximations. It is demonstrated that the use of adsorption constants for the evaluation of the concentration of adsorbed species is a strong approximation. Least squares fitting performed independently on each set of substrates with various approximations (6-10 parameters) showed surprisingly that, apart from the specific micro-kinetic constants of each substrate, compatible with their chemical structure, the fitting results converge to very similar values in the presence of different substrates for the kinetic constants of the semiconductor and those of the oxidant B (P25 and O_2). This result is encouraging, although it shows that analytically manageable macrokinetic models are affected by unavoidable (and somewhat critical) approximations.

References:

[1] Minero, C., Mariella, G., Maurino, V., Vione, D., Pelizzetti, E., Langmuir, 2000, 16(23), pp. 8964–8972

[2] Minero, C., Bedini, A., Maurino, V., Glycerol as a probe molecule to uncover oxidation mechanism in photocatalysis, Applied Catalysis B: Environmental, 2012, 128, pp. 135–143

[3] Minero, C., Vione, D., A quantitative evaluation of the photocatalytic performance of TiO2 slurries, Applied Catalysis B: Environmental, 2006, 67(3-4), pp. 257–269

Dissolution and photocorrosion protection of WO_3 electrodes by ALD coverage with TiO_2

Hana Krýsová[a*], Tomáš Imrich[a,b], Martin Brada[b], Hana Tarábková[a], Michael Neumann-Spallart[b], Josef Krýsa[b]

[a] J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences,
Czech Republic ([*] hana.krysova@jh-inst.cas.cz)
[b] Department of Inorganic Technology, University of Chemistry and Technology Prague,
Czech Republic.

Besides iron oxide in the form of hematite, another widely used n-type semiconductor metal oxide for photoelectrochemical applications is tungsten trioxide. Due to its higher bandgap (~2.7 eV) [1], the theoretical maximum energy conversion efficiency is lower (~12 %) but still significantly higher than that of TiO_2 (~4%). Hematite has low stability in acidic media ($pH \leq 2$) where it undergoes dissolution, while WO_3 has poor stability in alkaline media ($pH > 7$). TiO_2 or SnO_2 overlayers were used recently for increasing the stability of hematite photoanode in an acidic environment. Coverage of hematite by a very thin (2 nm) ALD TiO_2 film resulted only in a small decrease in photocurrent (in 0.1 M NaOH) (about 40 %), while the increase of the thickness to 8 nm led to almost complete suppression of the photocurrent (about 95 %). Exposure of uncovered hematite films to 0.01 M sulfuric acid led to a nominal dissolution rate of 7 pm/h. In addition to dissolution, a pH dependent alteration of the surface and photoelectrochemical corrosion took place. The Faradaic efficiency of this process was reduced from 0.026 % to 0.014 % when a 2 nm TiO_2 layer was applied [2,3].

In the present work WO_3 electrodes were covered with thin layers of TiO_2 in order to extend the range of operation in photoelectrochemical cells from the acid medium to higher pH. They exhibited a much smaller decrease in photocurrents when compared to TiO_2-covered α-Fe_2O_3 electrodes, where anodic photocurrents significantly decreased with increasing thickness of the ALD TiO_2 capping layers. The reason for this is ascribed to a more favourable relative position of valence band energies of the semiconductors WO_3 and TiO_2, allowing easier passage of photogenerated holes from the absorber material to the capping layer.

The presence of TiO_2 capping layers extended the chemical and photoelectrochemical stability range of WO_3 in contact with electrolytes up to pH 8 where an extension of the "lifetime" of photocurrents from 3 to 25 hours was observed for 20 nm thick TiO_2 capping layers. The efficiency of photocorrosion in pH 8 solutions decreased by a factor of 20 when the WO_3 electrodes were covered with TiO_2.

References:

[1] N.S. Gaikwad, G. Waldner, A. Brüger, A. Belaidi, S.M. Chaqour and M. Neumann-Spallart (2005). Journal of the Electrochemical Society, 152(5), p. G411.
[2] T. Imrich, H. Krýsová, M. Neumann-Spallart, J. Krýsa (2021). Journal of Electroanalytical Chemistry, 892, 115282.
[3] T. Imrich, M. Neumann-Spallart, H. Krýsova, H. Tarabkova, R. Nebel, J. Krýsa (2023). J. Photochem. Photobiol. A: Chem. 445, 115026.

Acknowledgements:

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

$SrTiO_3$: Fundamentals and Photocatalytic Applications

<u>Guido Mul,</u> Nathalia Costa, Tursun Abudukade, Igor Siretanu, Frieder Mugele,
Marco Altomare, Bastian Mei
University of Twente, Faculty of Science and Technology, Chemical Engineering Department,
MESA+ Institute for Nanotechnology, The Netherlands
(*G.Mul@utwente.nl)

Strontium titanate ($SrTiO_3$) is a perovskite-structured material with exceptional electronic and optical properties, making it a promising candidate for photocatalytic applications [1]. Moreover, $SrTiO_3$ allows preparation in specific crystallographic surface termination [2]. This presentation explores the fundamental aspects of $SrTiO_3$, including aqueous solvent and illumination-dependent changes in surface charges [3], which play a crucial role in its photocatalytic performance. Surface modifications, doping strategies, and heterojunction engineering have been widely investigated to enhance its photocatalytic efficiency, and will be addressed. Key applications include water splitting for hydrogen generation [1], and organic pollutant degradation [3], and will also be evaluated. Challenges such as surface affinity for chemisorption, charge recombination, and long-term stability are discussed alongside potential strategies for performance improvement. This lecture highlights recent advancements in understanding of $SrTiO_3$-based photocatalysis [3] and provides insights into future research directions for optimizing its efficiency in sustainable energy and environmental applications.

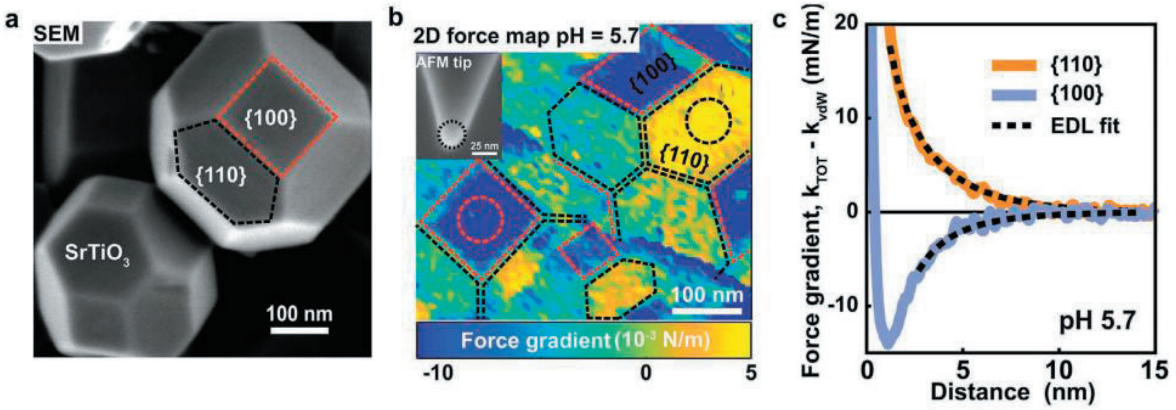


Figure 1: Illustration of the structure (a), facet specific charges in solution of pH 7 (b) and quantitative force-distance curves, confirming the negative charge of {110} surfaces (repulsive force), and positive charge of {100} facets (attractive force).

References:

[1] Han, K., Haiber, D.M. Knöppel, J., Lievens, C., Cherevko, S., Crozier, P., Mul, G., and Mei, B., ACS Catalysis 2021 11 (17), 11049-11058 - DOI: 10.1021/acscatal.1c03104

[2] Tavares Costa, N., Cunha, D.M., Zhu, K., Huijser, A., Katsoukis, G., Wenderich, K., Flapper, J., Mul, G., Energy Environ. Mater. 2024, 0, e12862 - DOI: 10.1002/eem2.12862

[3] Adv. Mater. 2021, 33, 2106229 - DOI: 10.1002/adma.202106229

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

Department of Chemical Engineering, Technion- Israel Institute of Technology, Haifa, Israel
paz@technion.ac.il

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, $BiVO_4$, 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 $Ti_{12}O_{15}$ 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 photo-catalytic 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.

SESSION VIII

Synergistic Catalyst Design and Mechanistic Insights for Enhanced Photocatalytic Urea Synthesis from CO_2 and N_2

Irfan Ahmad, Xie Quan*
Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education, China), School of Environmental Science and Technology, Dalian University of Technology, China

Photocatalytic synthesis of urea from co-reduction of CO_2 and N_2 under ambient conditions is an emerging and sustainable approach to chemical production, addressing both in energy and environmental impact of conventional Haber-bosh processes. However, this promising technology faces three fundamental challenges, (1) inefficient co-adsorption and competitive activation of CO_2 and N_2 on photocatalyst surface, (2) Sluggish C-N coupling kinetics, and (3) uncontrolled protonation of key intermediates. To overcome these limitation three breakthrough studies have systematically tracked through innovative photocatalyst design. Initially, competitive nature of CO_2 and N_2 on the same photocatalyst surface were resolved by engineering synergistic active sites on a diatomic Fe–Cu catalyst. Here, Fe sites preferentially adsorb and activate CO_2 while neighboring Cu sites stabilize N_2, enabling cooperative interaction and tailoring the C–N coupling site for efficient urea synthesis. Creating synergistic active centers that lower the energy barrier for *NCON intermediate, far surpassing the performance of isolated single-atom catalysts and individual Fe-Cu counterparts. This atomic-level cooperation enables exceptional urea yields of 12.45 $mg \cdot gcat^{-1} \cdot h^{-1}$ with 30.38% selectivity by overcoming the fundamental challenge of reactant competition. While the diatomic catalyst addresses adsorption challenges, the subsequent bottleneck of sluggish C─N coupling kinetics demands a solution of efficient and rapid charge transfer with a continuous supply of protons. This was achieved through a Z-scheme $SrTiO_3$-FeS-$CoWO_4$ heterostructure that spatially separates reduction sites while maintaining strong redox potentials. The FeS bridge critically enhances interfacial charge transfer, while dual active sites independently optimize CO_2 and N_2 adsorption. This design achieves record urea yields 8.05 $mg \cdot gcat^{-1} \cdot h^{-1}$ with 32.5% selectivity by simultaneously addressing charge recombination and providing sufficient electrons/protons for the C─N coupling. Finally, to prevent uncontrolled protonation of intermediates demands precise stabilization of reactive species to prevent undesirable byproducts. This was achieved through a strategic introduction of anionic sulfur vacancies in a $CsPbBr_3$-MoS_2-Pt plasmonic system that create electron-rich traps to stabilize critical *CO and *N_2 intermediates. The vacancies prevent premature protonation while plasmonic $CsPbBr_3$ ensures continuous high-energy electron supply, moreover Pt optimize proton delivery for selective hydrogenation. This synergistic approach achieves an outstanding urea yield of 16.10 $mg \cdot gcat^{-1} \cdot h^{-1}$ with 46.27% selectivity demonstrating how targeted vacancy engineering and co-catalyst loading can steer reaction pathways. These findings not only advance fundamental understanding of photocatalytic C-N coupling mechanisms but also provide a robust framework for designing next-generation photocatalysts for sustainable nitrogen fixation and carbon utilization. The insights gained may also extend to other challenging photocatalytic reactions requiring multi-step molecular transformations under mild conditions.

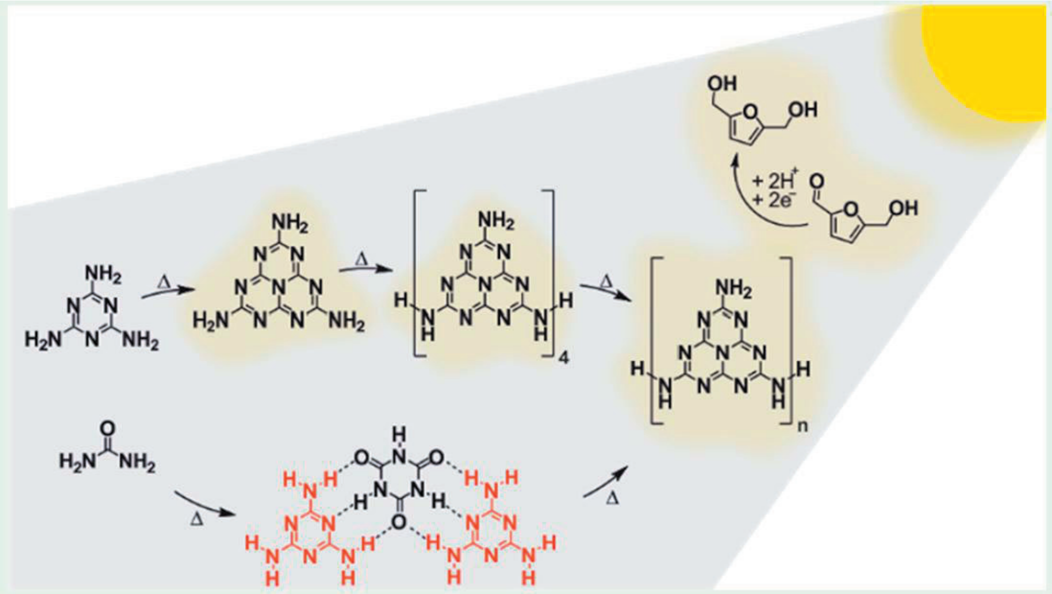
Enhancing the number of active amino groups in polymeric carbon nitride photocatalysts

Michael Wark, **Marco Weers, Thanh Thao Nguyen thi**

Institute of Chemistry, Chemical Technology 1, Carl-von-Ossietzky Universität Oldenburg, Germany

Polymeric carbon nitride (PCN) can be prepared by heating nitrogen-rich precursors and is used as a photocatalyst for hydrogen evolution and transformation of organic molecules. This work gives a deeper understanding of the different properties of PCN and the observed intermediates when melamine or urea are chosen as precursors and heated to temperatures in the range of 350–575 °C. Melem or a melem-tetramer are the main intermediates when melamine is used as starting material, while urea-based PCN is formed via a supramolecular assembly of melamine and cyanuric acid [1]. This leads to crucial differences in properties such as surface area, number of NH_2-groups and photocatalytic activity. PCN from urea, loaded with Pt nanoparticles, shows higher activities for photocatalytic hydrogen evolution due to more NH_2-groups. The melem-tetramer shows nanosheet-like structure combined with a high number of NH_2-groups and has the highest activity of all prepared catalysts for the photocatalytic reduction of 5-(hydroxymethyl)furfural (HMF) to 2,5-bis(hydroxymethyl)furan (BHMF). Thus, this research demonstrates the formation mechanism and the design of PCN based catalysts with a high number of NH_2-groups and a high photocatalytic reduction ability.

Additionally, some aspects regarding the use of PCN materials for presenting and discussing photocatalysis with pupils at school [2] will be given.



Reference

[1] M. Weers, A.R. von Seggern, H. Vocke, D.H. Taffa, M. Wark, ACS Appl. Nano Mater. 7 (2024) 1402-1415.

[2] M. Petersen1, J. Bauschulte, S. Talledo, K. Hotzel, M. Wark, K. Peneva, S. Bernhard, T. Wilke, J. Chem. Ed. (2025), accepted for publication.

SESSION IX

Ultrasound Induced Mineralization of Per- and Polyfluoroalkyl Substances (PFAS)

Xuexiang He*, Kevin E O’Shea*
Department of Chemistry and Biochemistry, Florida International University, United States.
*Corresponding authors:
Xuexiang He: hexa@mail.uc.edu
Kevin E O’Shea: osheak@fiu.edu

The limited effectiveness of conventional water treatment processes for the remediation of per- and polyfluoroalkyl substances (PFAS) in water has triggered intense investigation into the alternative advanced and novel technologies. We employed high frequency ultrasound irradiation (USI, at 396 W and 640 kHz) to remove PFAS with a specific focus on their mineralization into fluoride ions. Defluorination increased linearly with reaction time regardless of the studied PFAS species or experimental conditions. The order of percentage (%) defluorination rate followed PFOA ~ PFPeA ~ PFBA > 6:2 FTS > PFOS for the range of 10 – 50 μM. PFCAs appeared more susceptible to USI-based mineralization, consistent with the less thermal stability nature of PFCAs than other PFAS and our scavenging results revealing pyrolysis as the major mineralization mechanism. The F^- formation rates were 1.78 ± 0.23, 1.42 ± 0.15, 0.86 ± 0.04, 1.05, and 0.93 ± 0.15 μM min^{-1}, respectively, for the initial concentration 50 μM individual PFOA, PFPeA, PFBA, 6:2 FTS, and PFOS. Combined with the results on the impacts of different background matrices such as the high centration salt solutions or landfill leachates, we demonstrated that USI can be effective in PFAS mineralization in terms of defluorination.

What is the Environmental Risk of PFAS? How Can They Be Treated?

Zeynep Eren
Ataturk University, Engineering Faculty, Environmental Engineering Department, TÜRKİYE
*zeren@atauni.edu.tr

Per- and polyfluoroalkyl substances (PFAS), also known as “forever chemicals”, have been used in many industrial applications including fire retardants, textiles, surfactants, and food packaging. PFAS are a large, complex group of synthetic chemicals that have been used in consumer products include non-stick coatings, surfactants, food-packaging materials, and aqueous film-forming foams. For this reason, they are identified as being persistent, bio-accumulative, and having numerous potential adverse human and ecological impacts. PFAS have been widely used in many industrial sectors due to their hydrophobic, lipophobic, and thermostable properties that constitute a class of synthetic organic compounds formed through the partial or complete substitution of hydrogen atoms with fluorine atoms. The persistence of PFAS in the environment is mostly attributed to the remarkable stability of the carbon–fluorine (C-F) bond, which leads a resistance to classical water treatment methods. Consequently, there has been a remarkable increase in the release of PFAS to the environment due to the prevalence of PFAS extensively reported in various environmental matrices such as mainly surface water, and drinking water[1].

The inadequate and incomplete treatment of PFAS at wastewater treatment plants as well as the direct release of these substances through surface has a detrimental impact on water resources and poses a significant environmental risk for the safety of drinking water. Based on the reported data related to PFAS, it can be considered that its presence in vital organs of humans and other organisms is considered as toxic and dangerous[2,3]. The potential health hazards associated with PFAS result in various diseases such as ulcerative colitis, thyroid disorders, and cancer that affects both humans and other aquatic organisms. Recent investigations have reported an important relation between the presence of PFAS in human serum and their prevalence in drinking water. Therefore, the use of advanced oxidation processes (AOPs) such as photocatalysis, sonocatalysis, ozonation, Fenton oxidation has demonstrated promising outcomes in the degradation of PFAS. These techniques can be readily applied in classical water and wastewater treatment processes to remove PFAS.

Keywords: PFAS, Advanced Oxidation Processes, Micropollutants.

References:

[1]. Talabazar, F. R., Baresel, C., Ghorbani, R., Tzanakis, I., Koşar, A., Grishenkov, D., & Ghorbani, M. (2024). Removal of per-and polyfluoroalkyl substances (PFAS) from wastewater using the hydrodynamic cavitation on a chip concept. Chemical Engineering Journal, 495, 153573.

[2]. Qanbarzadeh, M., DiGiacomo, L., Bouteh, E., Alhamdan, E. Z., Mason, M. M., Wang, B., ... & Cates, E. L. Ersan, M. S., Wang, B., Wong, M. S., & Westerhoff, P. (2024). Advanced oxidation processes may transform unknown PFAS in groundwater into known products. *Chemosphere*, *349*, 140865.

[3]. Qanbarzadeh, M., DiGiacomo, L., Bouteh, E., Alhamdan, E. Z., Mason, M. M., Wang, B., ... & Cates, E. L. (2023). An Ultraviolet/Boron Nitride Photocatalytic Process Efficiently Degrades Poly-/Perfluoroalkyl Substances in Complex Water Matrices. *Environmental Science & Technology Letters*, *10*(8), 705-710.

Efficiency and mechanism of UV-based intermittent reductive/oxidative defluorination of PFOA&PFOS

S. Liu[1], H.H.M. Rijnaarts[1], R.C. Hofman-Caris[1,2], H. Bruning[1,*]
[1]Environmental Technology, Wageningen University and Research, the Netherlands
[2]KWR Water Research Institute, the Netherlands
(*harry.bruning@wur.nl)

Nowadays per- and polyfluoroalkylated substances (PFAS) have caused broad attention due to their widely existence in the environment, persistence, bioaccumulation, and potential health risks[1-5]. However, PFAS are highly resistant to conventional wastewater treatment due to their exceedingly stable C–F bonds[6, 7]. Through traditional reductive or oxidative destructive techniques, PFAS can be degraded but incomplete defluorination can cause the formation of fluorine-containing by-products with even greater toxicity[8, 9]. The produced fluorotelomers (C_nF_{2n+1}–$(CH_2)_m$–X) show high recalcitrance against further degradation during reductive defluorination processes[10, 11]. Hydroxyl radical (HO•) produced during oxidative processes can convert fluorotelomers into perfluorocarboxylates (PFCA)[12-14]. Based on this information, in this study, we propose an alternation of the UV/sulfite reductive process and the UV/H_2O_2 oxidative process to realize gradual degradation and defluorination of two typical PFAS, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). Combined with the literature[15-16], our results showed during UV/sulfite reductive process, there were two main degradation pathways. One the one hand, PFOA and PFOS could be gradually degraded into shorter-chain PFCA and perfluorosulfonic acids (PFSA) through the DHEH mechanism (Decarboxylation, Hydroxylation, Elimination, Hydrolysis). Meanwhile, the parent PFOA and PFOS, as well as the shorter-chain PFCA and PFSA produced during the DHEH mechanism, could also be further degraded into fluorotelomer carboxylic acids (FTCA) and fluorotelomer sulfonic acid (FTS) through the H/F exchange mechanism, which led to further defluorination. Then during the UV/H_2O_2 oxidative process, HO• transformed these fluorotelomers back to PFCA structure, which could be reduced by hydrated electron (e_{aq}^-) again in the following reductive process. Finally through the optimization of solution pH, sulfite and H_2O_2 dosages, and reaction time, we achieved 95% defluorination of 100 μg/L PFOA using a three-step redox process (3 h reduction, 3 h oxidation, and 2 h reduction), and 90% defluorination of 100 μg/L PFOS using a five-step redox process (2 h reduction, 20 min oxidation, 2 h reduction, 20 min oxidation, and 2 h reduction). To assess the practicality of the technology, we conducted the same experiment using tap water instead of demi water. The results showed that the higher ion and organic content in tap water would compete for ultraviolet light and free radicals, thereby affecting the defluorination efficiency. In this study, we achieved the intermittent reductive and oxidative conditions for the further defluorination of the recalcitrant toxic oxidation or reduction by-products, which might be a valuable strategy to consciously control the reaction process and the structure of intermediate products to realize deep defluorination. The results can give us new insights into the structure dependency of the defluorination mechanism, to help optimize degradation and defluorination strategies.

References:

[1] Buck, R.C., et al., (2011). *Integrated Environmental Assessment and Management*, 7(4), 513-541.
[2] Higgins, C.P., et al., (2005). *Environmental Science & Technology*, 39(11), 3946-3956.
[3] Naile, J.E., et al., (2010). *Environmental Pollution*, 158(5), 1237-1244.
[4] Giannetti, E., (2005). *Journal of fluorine chemistry*, 126(4), 623-630.
[5] Moore, J.T. and C.C. Lu, (2020). *Journal of the American Chemical Society*, 142(27), 11641-11646.
[6] Cui, J., P. Gao, and Y. Deng, (2020). Environ Sci Technol, 54(7), 3752-3766.
[7] Radjenovic, J., et al., (2020). Environ Sci Technol, 54(23), 14815-14829.
[8] Li, L., et al., (2017). *Environmental Science & Technology*, 51(8), 4461-4470.
[9] Bruton, T.A. and D.L. Sedlak, (2017). *Environmental Science & Technology*, 51(23), 13878-13885.
[10] Bentel, M.J., et al., (2019). Environ Sci Technol, 53(7), 3718-3728.
[11] Cheng, Z., et al., (2021). *Environmental Science & Technology Letters*, 8(8), 645-650.
[12] Houtz, E.F. and D.L. Sedlak, (2012). *Environmental science & technology*, 46(17), 9342-9349.
[13] Zhu, B., et al., (2019). *Environmental science & technology*, 53(9), 4823-4831.
[14] Zhang, Y., et al., (2020). *Environmental Science & Technology*, 54(7), 4631-4640.
[15] Liu, Z., et al., (2021). *Environmental Science & Technology*, 55(10), 7052-7062.
[16] Zhang, W., et al., (2023). *Journal of Water Process Engineering*, 53, 103836.

SESSION X

Nanoshaped plasmonic solids for heterogeneous photocatalytic applications

Albin Pintar
Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Slovenia

Plasmonic metals (e.g. Au, Ag) have an extremely large absorption/scattering cross section in the visible range and the ability to strongly focus light near their surface. Therefore, they may offer new opportunities to overcome the limited efficiency of TiO_2 and use it in various solar conversion devices such as photocatalysts and photovoltaic cells [1]. The underlying physical phenomenon for the enhanced visible-light interaction is based on localized surface plasmon resonance (LSPR). LSPR helps in the generation of electrons and holes. It is known that the hot electrons originate from the decay of LSPR and can be injected into the conduction band of TiO_2, which is known as hot electron injection process [2]. Thus, the combination of plasmonic metals with TiO_2 can enhance the light interaction of TiO_2 by scattering, absorption, sensitization and injection of hot electrons [3]. The plasmonic metals not only improve the light absorption by LSPR, but also form a Schottky barrier (SB) at the interface between the metal and the semiconductor. This SB can provide excellent charge separation in such nanostructures. The height of the Schottky barrier (SBH) is an important parameter that influences the efficiency of plasmon induced electron injection at the metal-semiconductor interfaces [4].
As a proof of concept, we have successfully fabricated free-standing immobilized TiO_2 and multi-segmented Au/TiO_2 nanorod arrays (NRAs) using a template-assisted electrodeposition technique. TiO_2 NRAs exhibit amorphous behaviour with strong absorption under UV light; transverse and longitudinal plasmon modes were observed for Au/TiO_2 NRAs under visible-light illumination. The Schottky barrier height (SBH) of 0.23 eV at the interface between the Au and TiO_2 segments was attributed to the high density of oxygen vacancies in the amorphous TiO_2. Photoelectrochemical measurements revealed an increased photoelectron generation of up to 400% in Au/TiO_2 NRAs, which was attributed to hot electron injection, plasmonic resonance energy transfer, and efficient charge separation/migration [5].

The same phenomena were demonstrated to occur in the presence of Au/TiO_2 nanorod particles [6,7]. By systematically synthesizing Au/TiO_2 nanorods with different Au loadings, keeping the morphological, structural and surface properties of the TiO_2 support constant, it was confirmed that the rate of a photocatalytic reaction (i.e. oxidation of water-dissolved bisphenol A) is directly influenced by the height of the Schottky barrier. It was demonstrated that the SB height decreases and the magnitude of the SPR effect increases as the diameter/amount of Au ensembles on the catalyst surface increases, and that both properties are essential to achieve high visible-light triggered catalytic activity of Au/TiO_2 catalysts. Recently, we have pioneered the synthesis of nanoflower-shaped Au photocatalysts (Au NFs) on TiO_2 nanorods (TNR) and systematically investigated their structural, optical and electronic properties [8]. Size- and shape-dependent LSPR effects were observed, which are reflected in the superior activity of the (Au NFs)/TNR photocatalyst for H_2-assisted NO_2 reduction at ambient conditions, compared to Au/TNR solids with spherical Au nanoparticles.

References:

[1] Z. Xuming, C. Yu Lim, L. Ru-Shi, T. Din Ping, Rep. Prog. Phys. 76 (2013) 046401; [2] X.-C. Ma, Y. Dai, L. Yu, B.-B. Huang, Light: Sci. Appl. 5 (2016) 16017; [3] W. Hou, S.B. Cronin, Adv. Funct. Mater. 23 (2013) 1612; [4] M.R. Khan, T.W. Chuan, A. Yousuf, M.N.K. Chowdhury, C.K. Cheng, Catal. Sci. Technol. 5 (2015) 2522; [5] M.S. Arshad, Š. Trafela, K. Žužek Rožman, J. Kovač, P. Djinović, A. Pintar, J. Mater. Chem. C 5 (2017) 10509; [6] G. Žerjav, J. Zavašnik, J. Kovač, A. Pintar, Appl. Surf. Sci. 543 (2021) 148799; [7] G. Žerjav, M. Roškarič, J. Zavašnik, J. Kovač, A. Pintar, Appl. Surf. Sci. 579 (2022) 152196; [8] Š. Slapničar, G. Žerjav, J. Zavašnik, M. Roškarič, M. Finšgar, A. Pintar, Molecules 29 (2024) 3333.

The Czech Society for Applied Photocatalysis: Activities and Opportunities

Jan Procházka
The Czech Society for Applied Photocatalysis, Czech Republic
Predseda.csaf@fotokatalyza.org

Photocatalysis is one of the rapidly developing fields within the domain of nanotechnology, an area that holds great promises for future advancements in environmental science and practical applications. The Czech Society for Applied Photocatalysis has been established by organizations utilizing the principles of photocatalysis. Companies and universities using various forms of photocatalyst, namely titanium dioxide, developing new technologies and products have created a professional framework and a certification program ensuring that these technologies and products meet specific technical parameters, thereby guaranteeing their functional properties, while complying with existing regulations on health protection, environmental conservation, and occupational safety.

Society's primary goal is to introduce a standards system that allows for the verification of the functionality of photocatalytic technologies. The certification program established by the society defines the requirements that the relevant technologies must meet, and the specific analytical methods needed to demonstrate compliance with standardized criteria. Obtaining the aforementioned certificate provides companies with a competitive market advantage and is compliant to the sustainability standards and ESG (Environmental, Social, and Governance reporting).

The CSAP certification program is open and available to all collaborating photocatalytic societies.

The presentation will introduce the Czech Society for Applied Photocatalysis as a whole, along with its individual members and their particular technologies.

Picture 1.

President of Asociación Ibérica de la Fotocatálisis David Almazan Cruzado and Jan Prochazka, president of the Czech Society of Applied Photocatalysis at the Milano Smart meeting at the Lombardy Chamber of Commerce.

Photocatalytic Titanium Dioxide in the Environmental Purification

Chiaki Terashima[1,2,3], **Hiroshi Uetsuka**[2,4], **and Katsuya Teshima**[2,3]
[1] Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Chiba, Japan
[2] Research Center for Space System Innovation, Tokyo University of Science, Chiba, Japan
[3] Institute for Aqua Regeneration, Shinshu University, Nagano, Japan
[4] Asahi Diamond Industrial Co., Ltd., Kanagawa, Japan
E-mail: terashima@rs.tus.ac.jp

Titanium dioxide (TiO_2) has been widely investigated as photocatalyst because of its environmentally and economically advantages with high chemical stability, earth abundant and biocompatible properties. However, its large band gap for the activity to only UV light region, and the high recombination rate of photogenerated electron and hole pairs have to be overcome to utilize effectively sunlight, and to enhance the photocatalytic performance. Recent enormous efforts to overcome the above-mentioned drawbacks have resulted in the one-dimensional TiO_2 nanotubes, nanofibers and nanorods to suppress the carrier recombination, and/or the heterojunction structure of TiO_2 with another semiconductor to achieve larger separation of the photogenerated electron and hole, as well as the modification of TiO_2 nanoparticles with gold clusters to expand the light conversion from UV to visible and near-infrared region. Another interesting approach on black TiO_2 nanoparticles succeeded in narrowing the band gap of pure white TiO_2 nanoparticles, however, it required the hard treatment condition of a 2 MPa hydrogen atmosphere at ca.200°C for 5 days (X. Chen, et al., *Science*, 331 (2011) 746).

To synthesize the hydrogenated TiO_2 nanoparticles, the thermal treatment under hydrogen and plasma treatment have mostly relied on the reduction of TiO_2 nanoparticles. But these processes have drawbacks such as high temperature over 1,000°C, vacuum system for hydrogen plasma and long treatment time. After thermal treatment, the sintered nanoparticles should be crush to follow multistep processes. Thus, alternative approaches have been highly demanded in the reduction of TiO_2 by keeping its nano-sized particle.

On the other hand, non-equilibrium plasma, in which the electron temperature is very high and deviates from the ion temperature, is an attractive reaction field because it can achieve low temperature processes in material synthesis and other applications. In particular, when plasma is generated in a liquid, reaction processes below the boiling point of the liquid become possible, and a special reaction field can be expected to be formed. In a so-called solution plasma using a bipolar pulse power supply (O. Takai, *Pure Appl. Chem.*, 80 (2008) 2003), the solvent was water, and plasma was generated in an air-fed environment within solvent. Therefore, the surface modification of TiO_2 nanoparticles in a solution plasma reaction field to introduce oxygen vacancy on the sub-surface while maintaining the nano-size has succeeded in improving photocatalytic activity (S. Pitchaimuthu, C. Terashima et al., *ACS Omega*, 3 (2018) 898). The present study focused on treating pristine TiO_2 nanoparticles by the discharge in water-based solution and to investigate the material properties as well as the photocatalytic activities for decomposing organics.

Unusual Radical Transformation Reactions as a Result of Light-Induced Ligand-to-Metal Charge Transfer of Iron Complexes

Christian Schöneich
Department of Pharmaceutical Chemistry, University of Kansas, USA

Iron complexes play an important role in the design of visible light-induced chemical transformations in organic chemistry. In proteins, such reactions can be confined to specific locations, depending on the nature of the iron binding site(s). In this way, the contamination of protein preparations with iron may cause unwanted protein degradation. We recently reported that iron binding to a monoclonal antibody (mAb) promoted site-specific cleavage through the oxidation of a single threonine (Thr) residue, induced by exposure to visible or near UV light. Mechanistically, this reaction required the oxidation of Thr to an intermediary alkoxyl radical. Extending this research to antibody fragments, we show here that visible and near UV light exposure does not only result in fragmentation at Thr but additionally promote a methyl transfer from Thr to an intermediary glycyl radical, ultimately resulting in the transformation of Thr to alanine (Ala). This methyl transfer strongly depends on the nature of the metal binding site and can be partially inhibited by the addition of other metal ions. Mechanistically, we propose that Ala is formed via multistep radical-radical coupling reaction, catalyzed by iron.

Thermo-photocatalytic removal of VOCs via TiO_2 supported on the nickel foam under UV-LED irradiation

Beata Tryba-*[1], **Maciej Trzeciak, Piotr Miądlicki**
Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology, Poland
e-mail: beata.tryba@zut.edu.pl

Volatile Organic Compounds (VOCs) are large group of chemicals that are one of the primary components of air pollution in many industries. They contribute significantly to greenhouse gases and are therefore subject to national and European directives. The photocatalytic processes can successfully decompose VOCs at ambient temperature and UV-Vis irradiation. However these processes are still less effective than catalytic or thermal oxidation of VOCs. Therefore recently some efforts are put on the development of complex systems of VOCs removal, which cover catalysis, photocatalysis and thermal decomposition. In the presented studies there are discussed results from the photocatalytic decompositions of acetaldehyde and ethylene conducted on TiO_2 supported on the porous Ni foam irradiated by UV-LED system. All the measurements were performed in a high-temperature reactor (The Praying Mantis™) equipped with the accessory for continuous in-situ FTIR measurements. These studies revealed enhanced photocatalytic performance of TiO_2, when was supported on Ni foam. At room temperature the conversion of acetaldehyde on TiO_2/Ni foam increased from 31 to 52%, but at 100ºC was double enhanced, from 40 to 85% [1]. Acetaldehyde mineralisation also increased at the presence of TiO_2 loaded on Ni foam. In case of ethylene, its decomposition was enhanced on TiO_2/Ni foam from 15% at room temperature to 30% at 50ºC and to 43% at 100ºC [2]. The performed photocatalytic tests of acetaldehyde and ethylene decompositions at the presence of some reactive scavengers indicated that superoxide anion radicals were dominant species contributing to their decompositions. It was stated that these species were greatly generated at the interfacial of TiO_2 and nickel foam. Therefore, at the presence of nickel foam, mineralization of both, acetaldehyde and ethylene were greatly enhanced.

Funding: National Science Centre, Opus 20, Grant No 2020/39/B/ST8/01514

References:

[1] Tryba, B.; Miądlicki, P.; Rychtowski, P.; Trzeciak, M.; Wróbel, R.J. The Superiority of TiO_2 Supported on Nickel Foam over Ni-Doped TiO_2 in the Photothermal Decomposition of Acetaldehyde. *Materials* **2023**, *16*, 5241. https://doi.org/10.3390/ma16155241

[2] Trzeciak, M.; Miądlicki, P.; Tryba, B. Enhanced Degradation of Ethylene in Thermo-Photocatalytic Process Using TiO_2/Nickel Foam. *Materials* **2024**, *17*, 267. https://doi.org/10.3390/ma17010267

SESSION XI

Photocatalytic Porous Coatings of Graphitic Carbon Nitride with Improved Adhesion Through Surface Preparation

S. Patakyová[1], P. Dzik[1]*
[1]Institute of Physical and Applied Chemistry, Faculty of Chemistry,
Brno University of Technology, Czech Republic
(**Sylvia.Patakyova@vut.cz*)

Graphitic carbon nitride (GCN) has emerged as a promising photocatalytic material due to its metal-free semiconductor properties, high thermal stability, and tunable electronic structure. GCN is composed of tri-s-triazine rings cross-linked by trigonal N atoms. The electronic band gap of GCN is approximately 2.7 eV, which is lower than that of the photocatalytic standard titanium dioxide (3.2 eV) [1]. Due to this property, GCN has the potential to react even within the visible light spectrum. However, optimizing its thin-film coatings for practical applications requires addressing challenges related to adhesion and porosity. Increasing the roughness of the substrate enhances mechanical interlocking, leading to stronger adhesion. A rough surface provides more anchoring points for the coating, creating a stronger physical bond. The increased surface area allows for more contact points between the photocatalytic layer and the substrate. Rougher surfaces can also aid in the formation of porous layers by improving the retention of pore-forming agents, which in turn enhances the photocatalytic activity of the prepared layers [2]. Incorporating porous structures into photocatalytic coatings enhances their performance by increasing surface area, improving light absorption, facilitating mass transport, and providing greater structural stability [3,4].

In our research, we explore the fabrication of porous GCN layers on modified substrates to improve mechanical stability and photocatalytic efficiency. The substrate surface was modified by laser engraving to create a rougher surface. The coatings were prepared using a wet ball-milled suspension of GCN, formulated with an oligomeric siloxane binder for adhesion control and camphor as a sacrificial pore-forming agent. The doctor blade technique was employed for deposition, followed by controlled sublimation of camphor under reduced pressure to introduce porosity.

Substrate modification was implemented to enhance adhesion properties. Structural and morphological analyses revealed that optimized porosity significantly improved light penetration and mass transfer, increasing photocatalytic activity. This work highlights the synergy between substrate surface engineering and tailored porosity in advancing the practical application of GCN coatings for environmental and energy-related technologies.

References:

[1] Polymeric Graphitic Carbon Nitride for Heterogeneous Photocatalysis | ACS Catalysis. https://pubs.acs.org/doi/10.1021/cs300240x

[2] Hot, J.; Topalov, J.; Ringot, E.; Bertron, A. Investigation on Parameters Affecting the Effectiveness of Photocatalytic Functional Coatings to Degrade NO: TiO2 Amount on Surface, Illumination, and Substrate Roughness. *International Journal of Photoenergy* **2017**, *2017* (1), 6241615. https://doi.org/10.1155/2017/6241615.

[3] Zhan, W.; Sun, L.; Han, X. Recent Progress on Engineering Highly Efficient Porous Semiconductor Photocatalysts Derived from Metal–Organic Frameworks. *Nano-Micro Lett.* **2019**, *11* (1), 1. https://doi.org/10.1007/s40820-018-0235-z.

[4] Wang, T.; Tian, B.; Han, B.; Ma, D.; Sun, M.; Hanif, A.; Xia, D.; Shang, J. Recent Advances on Porous Materials for Synergetic Adsorption and Photocatalysis. *ENERGY & ENVIRONMENTAL MATERIALS* **2022**, *5* (3), 711–730. https://doi.org/10.1002/eem2.12229.

Influence of Surface Charge and Functional Groups of Malachite Green and Methyl Red on Adsorption and Photocatalytic Degradation by Oxygen Vacancy-Enriched ZnO

Alireza Ranjbari[1,2], Philippe M. Heynderickx[1,2,*]
[1] Center for Green Chemistry and Environmental Biotechnology, Ghent University Global Campus, South Korea;
[2] Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Belgium.
*Philippe.Heynderickx@Ghent.ac.kr

Industrial dyes with cationic and anionic chromophores pose significant risks to the environment and human health. Cationic dyes like malachite green are toxic to aquatic life and potentially carcinogenic, while anionic dyes like methyl red disrupt ecosystems and induce oxidative stress. Due to their persistence and toxicity, effective remediation is crucial for environmental and public health protection [1].

Photocatalytic degradation (PCD) is an effective method for breaking down non-biodegradable contaminants like industrial dyes. This process relies on a photocatalyst, such as ZnO, which generates electron-hole pairs upon light activation. Introducing oxygen vacancies into metal oxide photocatalysts significantly enhances PCD performance by lowering the band gap, improving light absorption, and increasing active sites [2]. These vacancies serve as adsorption sites, strengthening dye attachment to the catalyst surface and influencing degradation pathways across different pH conditions. Additionally, they trap excited electrons, promoting electron transfer to adsorbed dye molecules and facilitating efficient degradation [2].

This study investigates how dye charge and functional groups, e.g., electron-donating and electron-withdrawing groups, influence adsorption and PCD using oxygen vacancy-enriched ZnO as a catalyst [3]. The oxygen vacancies were introduced via hydrogen reduction in a 10% H_2/Ar gas mixture at 500°C [2]. A comprehensive kinetic model was developed to account for reversible adsorption-desorption dynamics and differentiate between degradation by hydroxyl radicals in solution and electron-hole interactions on the catalyst surface. The model also incorporates dye speciation based on pK_a values to capture pH-dependent adsorption behavior [4]. Experimental findings reveal that maximum adsorption occurs at pH 3, where all dyes are fully protonated. Density functional theory (DFT) calculations, along with electrostatic potential (ESP) mapping, indicate that PCD predominantly takes place on the catalyst surface under acidic conditions, whereas in alkaline conditions, degradation shifts to the bulk solution. The results further highlight that cationic dyes with electron-donating groups exhibit the highest degradation rates at pH 11 due to their strong interaction with hydroxyl radicals, while anionic dyes with electron-withdrawing groups degrade most efficiently at pH 3 through electron-hole reactions on the catalyst surface. Lastly, quantum yield (QY) calculations show that cationic dyes reach a maximum QY of $7.12\ 10^{-5}$ at pH 11, whereas anionic dyes achieve their highest QY of $3.86\ 10^{-5}$ at pH 3.

References:

[1] A. Ranjbari, …, J. Yoon, P.M. Heynderickx, Chemosphere, 371 (2025) 144052.
[2] A. Ranjbari, …, P.M. Heynderickx, Appl. Catal., B, 324 (2023) 122265.
[3] A. Ranjbari, …, P.M. Heynderickx, Chem. Eng. J., 505 (2025) 159526.
[4] A. Ranjbari, …, P.M. Heynderickx, Chem. Eng. J., (2022) 133349.

TiO_2-EPS photocatalytic bed for acetaldehyde removal in the gas phase fluidized bed photoreactor

P. Rychtowski*, B. Prowans, P. Miądlicki, M. Trzeciak, B. Tryba
[1]Department of Catalytic and Sorbent Materials Engineering, West
Pomeranian University of Technology, Poland
*(*piotr.rychtowski@zut.edu.pl)*

Our recent studies have indicated that EPS (expanded polystyrene) is a suitable material for supporting TiO_2 in the preparation of a photocatalytic bed [1–3]. These studies employed a novel thermal method for the preparation of the photocatalytic bed, whereby EPS spheres coated with TiO_2 from an aqueous suspension were initially heated at 140°C for 6 hours. An alternative method involved the mixing of TiO_2 powder with EPS spheres, followed by heating at 140°C for 6 hours. Two types of TiO_2-based materials were utilized in the study: a commercial material (Degussa P25) and another prepared using raw titania material derived from the industrial processing (by the sulfur method) of titanium white. The materials obtained by thermal treatment were shrunk and demonstrated small size of diameter spheres with uniform TiO_2 coating. Photocatalytic tests were carried out in a photoreactor illuminated by high-efficiency UV LEDs, where a slightly elevated temperature was generated due to the high absorptivity of UV light by the bed coating. The optimum bed fill was 30%. In the case of lower bed fill, such as 15%, although acetaldehyde decomposition was high, instances of by-product decomposition were observed, e.g. acetic acid (as detected by gas chromatography).The combined photocatalytic and thermal effects resulted in the fantastic continuous purification of air containing high concentrations of acetaldehyde (800 ppm).Complete decomposition of acetaldehyde was observed even at high gas flow rates, such as 560 ml/min. The method of EPS coating under discussion is notable for its simplicity and its environmental friendliness. These properties are a result of the low temperature of preparation and the absence of toxic organic solvents. The economic benefits of these properties are also worthy of note.

Funding

This research was funded by the National Science Centre, Poland, grant no. 2020/39/B/ST8/01514.

References:

[1] Rychtowski, P.; Prowans, B.; Miądlicki, P.; Felczak, P.; Tryba, B. Enhanced Ethylene Removal in a Fluidized Bed Photoreactor with Polystyrene as a Novel Bed. *Ind. Eng. Chem. Res.* **2024**, *63*, 1802–1813, doi:10.1021/acs.iecr.3c03609.
[2] Rychtowski, P.; Miądlicki, P.; Prowans, B.; Tryba, B. High Performance Fluidized Bed Photoreactor for Ethylene Decomposition. *Pol. J. Chem. Technol.* **2022**, *24*, 50–56, doi:10.2478/pjct-2022-0014.
[3] Miądlicki, P.; Rychtowski, P.; Tryba, B. Coating of Expanded Polystyrene Spheres by TiO2 and SiO2–TiO2 Thin Films. *J. Mater. Res.* **2024**, *39*, 1473–1488, doi:10.1557/s43578-024-01319-3.

Preparation and characterization of TiO_2 nanorods@Ni-foam with *in situ* FTIR surface analyses during photocatalytic decomposition of acetaldehyde

P. Rychtowski*, B. Prowans, P. Miądlicki, M. Trzeciak, B. Tryba
[1]Department of Catalytic and Sorbent Materials Engineering, West Pomeranian
University of Technology, Poland
(*piotr.rychtowski@zut.edu.pl)

TNR@Ni-foam structures were prepared by an alkaline hydrothermal method consisting of two steps: (1) treatment of TiO_2 powder in autoclave in a strong alkaline medium (10 M NaOH) at 150ºC for 24h, then washing with 0.1 M HNO_3 and neutralization with deionized water, (2) hydrothermal treatment in autoclave at 180ºC for 24h. This method was chosen considering the possible dissolution of nickel foam in case of acid-hydrothermal process with HCl or other organic based syntheses [1]. A similar approach for TNR synthesis was reported elsewhere [2]. Two different TiO_2 samples were used for the preparation of TNR@Ni-foam: P25 with mixed anatase and rutile structures, produced by Evonik (Germany), and KRONO*Clean*®7050 with only anatase crystalline structure, produced by Kronos International (Germany).

TNR formation on the surface of Ni foam depended on the acid washing step of the formed layered titanate structure ($Na_2Ti_3O_7$). The optimum amount of HNO_3 used to substitute of Na^+ by H^+ and to form TNR was 10 ml for both TiO_2 samples used for preparation. After this process (acid washing), the $H_2Ti_3O_7$ structure was formed, as confirmed by XRD measurements. In the second step of the preparation, TiO_2 was crystallized by dehydration of $H_2Ti_3O_7$. In fact, anatase phase was crystallized for both samples with small amounts of brookite and rutile, however brookite and rutile were observed in higher amounts for P25 used for preparation. SEM images of the prepared TNR@Ni-foam structures indicated on the formation of vertical TNR on the Ni foam in the case of P25 and nano-flowers in the case of the anatase sample used. Interestingly, the prepared TNR@Ni-foam structures based on P25 contained Na residues regardless of the amount of HNO_3 used for washing, whereas no Na species were detected in case of TNR@Ni-foam obtained from anatase, as confirmed by XRFS analyses.

The resulting composites were tested at elevated temperature (100ºC) for acetaldehyde photodegradation (240 ppm in air) during continuous gas flow (5 ml/min) through the reactor coupled with FTIR. The results obtained revealed that TNR@Ni-foam structures prepared from P25 were more active than those obtained from the anatase sample KRONO*Clean*®7050.

Funding

This research was funded by the National Science Centre, Poland, grant no. 2023/49/N/ST11/01737.

References:

[1] Gupta, T.; Samriti; Cho, J.; Prakash, J. Hydrothermal Synthesis of TiO_2 Nanorods: Formation Chemistry, Growth Mechanism, and Tailoring of Surface Properties for Photocatalytic Activities. *Mater. Today Chem.* **2021**, *20*, 100428, doi:10.1016/j.mtchem.2021.100428.

[2] Xiong, J.; He, L. Influence of Na^+ Content on the Structure and Morphology of TiO_2 Nanoparticles Prepared by Hydrothermal Transformation of Alkaline Titanate Nanotubes. *J. Exp. Nanosci.* **2017**, *12*, 384-393, doi:10.1080/17458080.2017.1382734.

Optimized Crystallization of FA-Based Perovskite Light Absorber in Multiporous Layered Electrode Perovskite Solar Cells

T. Shioki[1], S. Oshita[1], N. Izumoto[1], S. Ito[1]*
[1]Department of Materials and Synchrotron Radiation Engineering, Graduate School of Engineering, University of Hyogo, Japan
*(*itou@eng.u-hyogo.ac.jp)*

Fully printable carbon-based multiporous layered electrode perovskite solar cells (MPLE-PSCs) are scalable, high stability and manufactured by using fully non vacuum processes [1-3]. Typically, $CH_3NH_3PbI_3$ ($MAPbI_3$) with 5−ammonium valeric acid iodide (5-AVA-$MAPbI_3$) has been used as the light absorbing material, but it leads to overestimated performance due to scan rate variations in current density-voltage (*J-V*) measurements [4]. This study introduces $CH(NH_2)_2$ (FA)-based perovskite material as an alternative material to address this issue and improve crystallization by optimization. The solar cells were fabricated by spray pyrolysis method for compact TiO_2 layer and screen printing to deposit mesoporous layers (TiO_2, ZrO_2 and carbon). As the results, the solar cells using $RbCsFAPbI_3$ suppressed the variation of current density for low-speed scanning, compared with 5-AVA-$MAPbI_3$.

References:

[1] Mei A. Li X. Liu L. Ku Z. Liu T. Rong Y. Xu M. Hu M. Chen J. Yang Y. Grätzel M. & Han H. (2014). *Science*, 345 295–298
[2] Baranwal AK. Kanda H. Shibayama N. Masutani H. Peiris N. Kanaya S. Segawa H. Miyasaka T. & Ito S. (2019). *Energy Technology,* 7 (2), 245–252
[3] Kobayashi E. Tsuji R. Martineau D. Hinsch A. & Ito S. (2021). *Cell Reports Physical Science,* 2 (12)
[4] Perrin L. Planes E. Shioki T. Tsuji R. Honore J.C. Farha C. Ito S. & Flandin L. (2024). *Solar RRL,* 8 (17), 2400393

The Urbach energy as an important parameter in material optimization

L. Svoboda[1,*], Z. Vilamová[1], P. Praus[2,3], J. Bednář[1], Z. Šimonová[4], R. Dvorský[4]
[1]Nanotechnology Centre, Centre for Energy and Environmental
Technologies, VSB – Technical University of Ostrava, Czech Republic
[2]Department of Chemistry and Physico-Chemical Processes, VSB – Technical University of
Ostrava, Czech Republic
[3]Institute of Environmental Technology, Centre for Energy and Environmental Technologies,
VSB – Technical University of Ostrava, Czech Republic
[4]Centre for Advanced Innovation Technologies, Faculty of Materials Science and
Technology, VSB – Technical University of Ostrava, Czech Republic
*ladislav.svoboda@vsb.cz

The Urbach energy (E_U) is a mostly overlooked parameter that provides a deeper understanding of the optical properties of graphitic carbon nitride (g-C_3N_4) as it indicates structural disorder and localized states in the bandgap. A higher E_U suggests an increased defect density, affecting electronic transitions and absorption properties. These defects influence charge carrier dynamics, optical absorption, and overall material efficiency in various applications, including optoelectronics and photocatalysis [1].

The so-called Urbach tail represents the exponential absorption edge where localized states extend into the bandgap due to lattice imperfections. In g-C_3N_4, increased E_U values indicate enhanced disorder. These defects alter the band structure, impacting optical absorption and photocatalytic efficiency. Structural defects can either improve charge carrier separation or act as recombination centres, reducing performance. The presence of defect states can also contribute to bandgap narrowing, leading to enhanced light absorption and improved photocatalytic activity in some cases.

The relationship between Urbach energy and structural disorder varies with the potassium precursor [1]. KOH-modified g-C_3N_4 exhibits a linear E_U trend, while KCl-modified samples show a two-step increase, suggesting distinct defect formation mechanisms. This variation influences bandgap narrowing and charge carrier dynamics. The precursor choice significantly impacts the Urbach tails, further influencing the electronic structure and optical behaviour of g-C_3N_4.

While moderate disorder enhances absorption and catalytic activity, excessive defects increase recombination rates. For instance, TiO_2 thin films with lower Urbach energy exhibit higher photocatalytic activity, emphasizing the need for optimized defect engineering [2]. Similarly, Cu-doped ZnO photocatalysts show improved degradation activity within an optimal E_U range [3]. However, an uncontrolled increase in Urbach energy may lead to decreased performance due to excessive defect states acting as recombination centres.

The impact of Urbach energy extends beyond photocatalysis, as structural disorder also affects other optoelectronic applications such as light-emitting diodes (LEDs) and photodetectors [4,5]. The presence of localized defect states influences carrier transport and luminescence properties, making Urbach energy a crucial factor in material optimization. By tailoring structural disorder and managing defect densities, researchers can enhance the optical performance of devices.

In summary, controlling Urbach energy in photocatalytic materials is essential for tuning optical properties. While structural defects can improve performance, excessive disorder hinders efficiency. The choice of precursor plays a significant role in determining the extent of structural disorder and its influence on the electronic structure. A balanced approach to defect formation is key to optimizing g-C_3N_4 for photocatalytic and optoelectronic applications, ensuring improved absorption, charge carrier dynamics, and overall material functionality.

References:

[1] Svoboda L., Vilamová Z., Praus P., Novák V., Kutláková M.K., Petr M., Bednář J., Jochim V., Šimonová Z. & Dvorský R. (2025). *Applied Surface Science*, 279, 161162

[2] Rahman H.K. & Kar K.A. (2019). *Materials Research Express* 6 (9), 096436

[3] Janani Archana K., Christy Preetha K. & Balasubramanian K. (2022). *Optical Materials* 127, 112245

[4] Kumar A., Ravina A., Kumar V., Deopa N., Punia R. & Rao A.S. (2023). *Materials Letters: X* 19, 100210

[5] Dalal A., Mishra M., Chakrabarti S., Gupta R.K. & Mondal A. (2022). *Vacuum* 201, 111115

Application of Metallic Foams and Titanium Dioxide Composites for Photocatalytic Removal of Volatile Organic Compounds

Maciej Trzeciak*[1], **Bartłomiej Prowans**[1], **Beata Tryba**[1]
Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology, Poland
e-mail: maciej.trzeciak@zut.edu.pl

Volatile organic compounds (VOCs) are a significant class of air pollutants with adverse effects on both human health and the environment. Their effective removal from the atmosphere remains a critical challenge. Composites of metallic foams and titanium dioxide (TiO_2) present a promising solution for the photocatalytic degradation of VOCs due to their synergistic properties and structural characteristics. Metallic foams, with their high porosity, large surface area, and excellent mechanical stability, serve as an ideal substrate for supporting photocatalytic materials. TiO_2, a widely recognized photocatalyst, is well-known for its high reactivity under UV light, but its performance can be further enhanced when is integrated with nickel foam [1]. There are some reports showing that nickel foam could retard recombination of free charges in TiO_2 during photocatalytic process and thereby boosting its photocatalytic activity [2]. However, for now only nickel foam was explored as a metallic foam used in the composites with TiO_2 or other photocatalysts. Currently, there is limited knowledge regarding the use of various metallic foams coupled with TiO_2. In these studies the composites consisted of various metallic foam (Ni, Co, Fe, Cu) and TiO_2 will be tested for the photocatalytic degradation of acetaldehyde. Moreover, thermo-photo-catalytic processes will be applied, to investigate impact of temperature, catalyst and light for the acceleration of acetaldehyde decomposition. These measurements will be conducted in a high-temperature reactor (The Praying Mantis™) under UV-LED irradiation ($\lambda = 365$ nm), with in-situ FTIR surface analysis. The system of continuous flow of gas through the reactor will be applied with simultaneous analyses of acetaldehyde concentration in gas chromatograph and CO_2 concentration in CO_2 analyser. The important material analyses such as: SEM/EDS, XPS, XRD and UV-Vis/DR will be used to investigate the structural, chemical and optical properties of the prepared composites.

Funding: National Science Centre, Opus 20, Grant No 2020/39/B/ST8/01514

References:

[1] Tryba, B.; Miądlicki, P.; Rychtowski, P.; Trzeciak, M.; Wróbel, R.J. The Superiority of TiO_2 Supported on Nickel Foam over Ni-Doped TiO_2 in the Photothermal Decomposition of Acetaldehyde. *Materials* **2023**, *16*, 5241. https://doi.org/10.3390/ma16155241

[2] Hu, H.; Xiao, W.; Yuan, J.; Shi, J.; Chen, M.; Shang Guan, W. Preparations of TiO_2 Film Coated on Foam Nickel Substrate by Sol-Gel Processes and Its Photocatalytic Activity for Degradation of Acetaldehyde. *J. Environ. Sci.* **2007**, *19*, 80–85

Material Printing of Indicators Based on Photochemical and Photocatalytic Principle

M. Veselý, V. Dobiáš, D. Filipi, P. Dzik
Brno University of Technology, Faculty of Chemistry, Czech Republic,
michal.vesely@fch.vut.cz

Although the Earth's atmosphere significantly reduces incident radiant power in the most harmful spectral bands, overexposure of untrained and/or unprotected human skin to solar radiation can easily lead to acute and chronic adverse effects on human skin. We report on the design, development, laboratory-scale fabrication, calibration, and manufacture of photosensitive indicators for personal monitoring of user exposure to solar radiation. Two types of indicators are discussed, whose photosensitive component is titanium dioxide and changes its colour upon interaction of hydroxyl radicals generated on the surface of titanium dioxide photocatalyst nanoparticles to the dye present. The former was prepared as highly sensitive with a response to erythemal radiation doses of 1 and 2 SED, while the latter is less sensitive with a response to doses of 3 and 4 SED. An additional radiation dose indicator, sensitive only to UVB radiation, has also been developed to monitor UVB phototherapy. The photochemical reactions leading to the colour change of the indicator will be described. The UVB indicator has been prepared by printing the material using a screen-printing technique.

Another indicator showing a colour change in the presence of oxygen has been developed for applications in smart food packaging. The indicator was printed on plastic film and covered with a UV curable coating. After activation of the indicator by UVA radiation by photocatalytic reduction of the dye present in the absence of oxygen, the indicator is ready to react with oxygen by changing colour. Data for the kinetic study of photocatalytic reduction and oxidation were collected using a reflectance spectrophotometer and the kinetic analysis was based on the change in optical density of the indicator. The indicator wase successfully printed by rotary screen printing technique.

References:

[1] Veselý M., Dzik P., Ettler K., Wertzová V., Kubáč L., Klusoň P.: J. of Photochemistry & Photobiology, A: Chemistry 454, (2024), 115741
[2] Dobiáš V., Filipi D., Veselá M., Krčma F., Veselý M.: J. of Photochemistry & Photobiology, A: Chemistry 455, (2024), 115762

Printed Photoelectrochemical Cells for Sensing, Remediation and Energy Harvesting

P. Dzik, M. Veselý
Brno University of Technology, Faculty of Chemistry, Brno, Czech Republic,
dzik@fch.vut.cz

A photoelectrochemical cell is a device where at least one working electrode consists of a semiconductor supported on an electrically conductive substrate. The photocatalytic activity of immobilized semiconductor photocatalysts can be enhanced by applying an external electrical bias, which improves electron–hole separation and increases the quantum yield of redox reactions at the electrodes. This enhancement requires the photocatalyst to be deposited on a conducting substrate. In n-type semiconductors, the working electrode functions as a photoanode with a positive bias, typically comprising a conducting base coated with a semiconducting metal oxide like titanium dioxide. The counter electrode's material must offer adequate electrical conductivity and corrosion resistance.

The photocurrent produced in an irradiated cell depends on factors such as electrolyte composition, irradiance, electrode materials, and cell design. These cells can be used for diverse applications, including sensing, remediation, and energy harvesting.

Material printing is an emerging microfabrication technique suitable for producing planar layered devices, such as photoelectrochemical cells. It involves sequentially layering patterned functional materials using modified traditional printing methods. Among these, inkjet printing holds a prominent position due to its versatility. Despite constraints like viscosity and particle size, it is ideal for lab-scale prototype development since it eliminates the need for hardware printing forms. Patterns designed digitally can be printed directly, and the process is easily scalable to industrial levels using large-scale inkjet printers.

This study adopts the concept of planar electrochemical cells and integrates it with material printing for rapid processing and scalability. The method enables the printing of essential materials, including insulating, semiconducting, and conducting layers. The potential applications of these cells—sensing, remediation, and energy harvesting—are discussed alongside their physical, electrochemical, and photocatalytic properties.