# Second Solar Chemicals Network Symposium

# Programme and Abstract Booklet

# 13<sup>th</sup> and 14<sup>th</sup> January 2025

# **Event information**

The symposium will be held in the B10 Lecture Theatre at the Molecular Sciences Research Hub (MSRH) at the White City Campus of Imperial College London.



View of the Molecular Sciences Research Hub (MSRH), White City Campus, Imperial College London

Information on how to reach the White City Campus can be found here: <u>https://www.imperial.ac.uk/white-city-campus/about-us/how-to-find-us/</u>

When you arrive at the building during the morning registration period, you will be greeted and guided to the symposium location - **B10 Lecture Theatre**. If you arrive outside registration time, please ask for directions at the building reception.

Please note that you will need to sign in at the reception desk to get admission to the building, which is otherwise only accessible by college ID card. Hence, please allow some time for this.

# Programme

# Monday, 13<sup>th</sup> January

10:00 - 10:25	Refreshments and registration		
10:25 – 10:30	Welcoming remarks		
10:30 – 11:15	Invited talk: Rewiring photosynthesis using an electrochemist's toolbox		
	Jenny Zhang, University of Cambridge		
11:15 – 11:35	Synthetic and biological photoelectrocatalysts for solar chemicals		
	Yongpeng Liu, University of Cambridge		
11:35 – 11:55	Sustainable co-production of hydrogen and value-added chemicals with		
	waste electrolysis		
	Hui Luo, University of Surrey		
11: 55 – 12: 15	Photocatalytic hydrogen production coupled to glucose oxidation to value		
	added gluconic acid using a conjugated polyelectrolyte photocatalyst		
	Rhys Bourhill, University of Strathclyde		
12:15 – 13:20	Lunch + Posters		
13:20 – 14:05	Invited talk: Carbon dioxide electrolysis for defossilisation of plastic		
	production		
	Charlie Creissen, Keele University		
14:05 – 14:25	Direct air carbon capture for solar chemicals synthesis		
	Sayan Kar, University of Cambridge		
14:25 – 14:45	The effect of Zr on Bi electrocatalyst for enhancing CO <sub>2</sub> conversion to		
	Juntae Song, Kyushu University		
14:45 – 15:15	Coffee Break		
15:15 – 15:35	Investigating cation-dependent water oxidation kinetics on iridium based		
	Yemin Tao, Imperial College London		
15:35 – 15:55	Synergistic effect of multifold smart composite for the self-cleaning and energy-saving built environment		
	Anurag Roy University of Exeter		
15:55 – 16:40	Invited talk: Developing devices and characterisation tools for efficient and stable photoelectrochemical cells based on earth-abundant materials		
	Eluria Eiener Oucer Mary University of Lender		
	Fiurin Eisner, Queen Mary University of London		
16:40 – 18:00	Reception + Posters		

# Tuesday, 14<sup>th</sup> January

08:30 - 09:00	Refreshments		
09:00 - 09:45	Invited talk: Light optimization methods for high rate photocatalysis		
	Katie Shanks, University of Exeter		
09:45 – 10:05	Photocatalysis with metallic nanoparticles		
	Johannes Lischner, Imperial College London		
10:05 – 10:25	Chalcogenide thin film photocathodes for photoelectrochemical hydrogen		
	Valentina Corsetti University of Bristol		
10:25 - 10:45	Mechanistic insights to photo-physical processes and light-driven ionics in		
10.20 10.40	organic based semiconductors for efficient photocatalytic hydrogen		
	evolution		
	Filip Podjaski, Imperial College London		
10:45 – 11:15	Coffee break		
11:15 – 12:00	Invited talk: Transition metal oxides: passivating layers, electrocatalysts, photoelectrodes?		
	David Fermin, University of Bristol		
12:00 – 12:20	Spectroscopic measurements of quasi-Fermi level splitting in Fe <sub>2</sub> O <sub>3</sub>		
	Louise Oldham, Imperial College London		
12:20 – 12:40	Cation-enhanced nitrogen reduction studies with a photoelectrochemical p- InP-CoMo system		
	Manpreet Kaur, University of Warwick		
12:40 – 13:00	A carbon cathode for lithium mediated electrochemical ammonia synthesis		
	Craig Burdis, Imperial College London		
13:00 – 14:15	Lunch + Posters		
14:15 – 15:00	Invited talk: Approaches to enhance hematite performance for photoelectrocatalytic water oxidation		
	Ana Sobrido, Queen Mary University of London		
15:00 – 15:20	Design strategies for reducing charge recombination in polymer photocatalysts and photoelectrodes		
	Sam Hillman, Imperial Collee London		
15:20 – 15:40   Revolutionizing solar efficiency: Al-driven performance assessme amorphous thin film solar cells with non-transparent and transpar electrodes			
	Ziad Khalifa, The British University in Egypt		
15:40 - 16:00	16:00 Impact of cobalt intercalation on the electrochemical properties of layered birnessite under water oxidation potentials		
	Sid Halder, Imperial College London		
16:00 – 16:30	Poster awards + close		

# Abstracts

# Rewiring photosynthesis using an electrochemist's toolbox

Jenny Zhang

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Abstract

The 'light reaction' of biological photosynthesis generates high-energy electron vectors to enable reactions such as the fixation of carbon dioxide and nitrogen in nature. The biohybrid community can now wire into the photosynthetic electron transport chain, both in vitro and in vivo, with the outlook to promote various bioenergetic pathways and create new clean energy conversion solutions.[1]

In this talk, I will show my team's latest efforts to re-wire biological photosynthesis using an electrochemist's toolbox. In particular, our work challenges existing design rationales for enhancing photosynthesis and biohybrid systems using 3D-structured electrodes, electron mediators, and by manipulating the bio-material interface. This work showcases the enormous interdisciplinary opportunities in this space for diversifying and strengthening solar chemical generation strategies.

**Biography** 



Dr Jenny Zhang was appointed as Assistant Professor at the Yusuf Hamied Department of Chemistry, University of Cambridge, after starting her group developing semi-artificial photosynthesis six years ago as a BBSRC David Phillips Fellow. She has a highly dynamic interdisciplinary research group that blends electrochemistry with biology, physics and materials science, and her work on semi-artificial photosynthesis has led to awards such as the Felix Frank Biotechnology Medal, the Loreal-UNESCO Women in Science Award in Sustainability Development, and the ERC Consolidator Award. She is presently the Deputy Director of the UK Solar Chemicals Network.

# Synthetic and biological photoelectrocatalysts for solar chemicals

Yongpeng Liu

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#### Abstract

Converting solar energy into clean chemical fuels using  $H_2O$  and  $CO_2$  as feedstock is a key strategy for achieving a carbon-neutral society. The assembly of semiconductors as light absorbers and enzymes as redox catalysts offers a promising approach for sustainable chemical synthesis driven by light. However, the rational design of such semi-artificial systems requires a comprehensive understanding of the abiotic-biotic interface, which poses significant challenges.<sup>[1-3]</sup>



Figure 1: Solar fuel synthesis using a semiartificial colloidal Z-scheme.<sup>[1]</sup>

This presentation will showcase our recent advancements in the development of novel semiconductors and the construction of bio-hybrids for solar chemical applications, employing photoelectrochemistry and photocatalyst approaches. Emerging semiconducting materials such as carbon nitrides,<sup>[2]</sup> CulnGaS<sub>2</sub>,<sup>[4,5]</sup> ZnFe<sub>2</sub>O<sub>4</sub>,<sup>[6]</sup> CuFe<sub>2</sub>O<sub>4</sub>,<sup>[7]</sup>  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,<sup>[8,9]</sup> and LaFeO<sub>3</sub><sup>[10]</sup> have been explored for direct solar H<sub>2</sub> production and CO<sub>2</sub> conversion, complemented by a set of spectroelectrochemistry such as intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS), photoelectrochemical impedance spectroscopy (PEIS) and operando Raman/UV-Vis spectroscopy. Our findings contribute to the ongoing efforts in addressing the challenges associated with the abiotic-biotic interface in the rational design of efficient and selective solar-driven chemical synthesis systems.



Figure 2: Photoelectrochemical CO<sub>2</sub> reduction at a direct CulnGaS<sub>2</sub>/electrolyte junction.<sup>[4]</sup>

- 1. **Y. Liu**, A. B. M. Annuar, S. R.-Jiménez, C. W. S. Yeung, Q. Wang, A. M. Coito, R. R. Manuel, I. A. C. Pereira, E. Reisner. *J. Am. Chem. Soc.* **2024**, *146* (43), 29865-29876.
- Y. Liu, C. Pulignani, S. Webb, S. J. Cobb, S. Rodríguez-Jiménez, D. Kim, R. D. Milton, E. Reisner. *Chem. Sci.* 2024, 15 (16), 6088-6094.
- 3. Y. Liu, S. Webb, P. Moreno-García, A. Kulkarni, P. Maroni, P. Broekmann, R. D. Milton. *JACS Au* 2023, 3 (1), 124-130.
- Y. Liu, M. Xia, D. Ren, S. Nussbaum, J.-H. Yum, M. Grätzel, N. Guijarro, K. Sivula. ACS Energy Lett., 2023, 8 (4), 1645-1651.
- 5. Y. Liu, M. Bouri, L. Yao, M. Xia, M. Mensi, M. Grätzel, K. Sivula, U. Aschauer, N. Guijarro. *Angew. Chem. Int. Ed.* 2021, *60* (44), 23651–23655.
- 6. Y. Liu, M. Xia, L. Yao, M. Mensi, D. Ren, M. Grätzel, K. Sivula, N. Guijarro. Adv. Funct. Mater. 2021, 31 (16), 2010081.
- 7. Y. Liu, F. Le Formal, F. Boudoire, L. Yao, K. Sivula, N. Guijarro. J. Mater. Chem. A 2019, 7(4), 1669–1677.
- 8. Y. Liu, N. Guijarro, K. Sivula. Helvetica Chimica Acta 2020, 103 (6), e2000064.
- 9. Y. Liu, F. Le Formal, F. Boudoire, N. Guijarro. ACS Appl. Energy Mater. 2019, 2, 6825–6833.
- 10. **Y. Liu**, J. Quiñonero, L. Yao, X. D. Costa, M. Mensi, R. Gómez, K. Sivula, N. Guijarro. *J. Mater. Chem. A* **2021**, *9* (5), 2888–2898.

# Sustainable co-production of hydrogen and value-added chemicals with waste electrolysis

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### Abstract

In the transition towards Net-Zero, there is significant interest in phasing out fossil fuels as both the energy source and precursor for petrochemicals. Biomass is recognised as an ideal  $CO_2$  neutral, abundant and renewable resource substitute to fossil fuels. The rich proton content in most biomass derived materials endows it to be an effective hydrogen carrier.<sup>1</sup> The inherent chemical structure allows them to be easily catalysed to produce valuable commodity chemicals that can be used in applications such as biodegradable polymers and pharmaceuticals. Although historically biomass has been regarded as waste stream, recent years have seen increasing attentions in valorising it into useful products.

In this talk, I present biomass electrolysis, specifically glycerol (the waste by-product from bio-diesel industry), as an alternative route to produce hydrogen and value-added chemical, lactic acid. The process resembles water electrolysis, with H<sub>2</sub> produced on the cathode via hydrogen evolution reaction. On the anode, however, instead of oxidising water, a combined electrochemical & chemical process take place that transforms glycerol into lactic acid. Here I present the fundamental knowledge on how a multi-component tandem catalyst system Pt/C-Al<sub>2</sub>O<sub>3</sub> can tune the selectivity towards lactic acid,



Figure 1: illustration of waste electrolysis

**References** 

- 11. <u>H. Luo</u>, J. Barrio, N. Sunny, A. Y. Li, L. Steier, N. Shah, I. E. L. Stephens, M. M. Titirici, Adv. Energy. Mater., 2021, 2101180
- 12. <u>H. Luo,</u> M. Xu, S. Liu, G. Tarantino, H. Ye, H. Yadegari, A. Y. Li, C. Hammond, G. Kastlunger, I. E. L. Stephens, M. M. Titirici, EES Catal., DOI: 10.1039/D4EY00236A.
- 13. M. Aslam, M. Navlani-Garcia, D. Cazorla-Amoros, <u>H. Luo</u>, J. Phys. Mater., 2023, 7(1), 015002.

acquired through advanced material characterisations and DFT calculation.<sup>2,3</sup> At the same time, details on catalyst requirements and recent advances for future strategic design of the processing system will be provided.

Looking beyond, an even more abundant and low-value waste stream than biomass is plastic. Finding a way to upcycle plastic derivatives become imperative to help tackle this global challenge. Therefore, the last part of my talk will share our recent studies on PET (polyethylene terephthalate) derived ethylene glycol (EG) electrolysis to co-produce hydrogen and glycolic acid. Au based nanoparticle electrocatalyst has been used to drive the reaction at Ampere-scale with > 85% glycolic acid selectivity, revealing its high potential in industrial relevant applications.

# Photocatalytic hydrogen production coupled to glucose oxidation to value added gluconic acid using a conjugated polyelectrolyte photocatalyst

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# Abstract

Photocatalysts can enable the production of hydrogen from water using solar light through water splitting. However, the water oxidation half reaction is kinetically and thermodynamically challenging and therefore in most cases sacrificial agents are added to discourage exciton recombination and improve the efficiency of the proton reduction half-reaction.<sup>1</sup> The use of a sacrificial agent also allows for the production of value-added products from the corresponding oxidation reaction instead of the oxygen produced by water splitting. However, commonly used sacrificial agents such as triethylamine are petrochemically derived compounds, are toxic and are typically oxidised into non-useful waste products, making the overall process unsustainable.<sup>2</sup> Utilising abundantly available biomass such as glucose as a sacrificial hole scavenger allows for an overall more sustainable process while also being oxidised more easily than water into potentially useful products.<sup>3</sup> By utilising a conjugated polyelectrolyte photocatalyst with ionic ammonium side chains alongside glucose, hydrogen was successfully produced at a rate more than double that obtained when using triethylamine as a scavenger and tenfold higher than that observed when an analogous non-ionic conjugated polymer is used. This indicates that there is a significant unique interaction between charged polymer side chains and glucose that does not occur with triethylamine. Furthermore, glucose was successfully oxidised into gluconic acid (88%) and mannitol (12%) which have uses in the construction and medical industries respectively. This work highlights the unique enhancement of photocatalytic hydrogen production when using a conjugated polyelectrolyte photocatalyst with glucose as a more sustainable scavenger over typical tertiary amine scavengers.





# <u>References</u>

- 1. Nishioka, S. et al. Photocatalytic water splitting. Nat Rev Methods Primers 3, 1–15 (2023).
- 2. M. Aitchison, C. *et al.* Structure–activity relationships in well-defined conjugated oligomer photocatalysts for hydrogen production from water. *Chemical Science* **11**, 8744–8756 (2020).
- 3. Davis, K. A. *et al.* Photocatalytic hydrogen evolution from biomass conversion. *Nano Convergence* **8**, 6 (2021).

# Carbon dioxide electrolysis for defossilisation of plastic production

# Charles E. Creissen

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#### Abstract

Plastics are essential to modern life, but their production from fossil fuels generates significant greenhouse gas emissions. A sustainable solution to bypass this issue is  $CO_2$  electrolysis, in which renewable electricity is used to power the production of plastic precursors. However, guiding these reactions towards desired products at high reaction rates requires combined efforts in chemistry, materials, and engineering. In this talk, I will highlight recent work to enhance selectivity, conversion, and efficiency of devices for high-rate  $CO_2$  electrolysis. This will include consideration of catalyst surfaces, the use of acidic conditions to bypass parasitic  $CO_2$  conversion to (bi)carbonate, and the impact of cell configuration and components on the full-cell voltage.

#### **Biography**



Charlie obtained his PhD from the University of Cambridge in 2019 and subsequently undertook Postdoctoral Research Associate and Research Engineer positions at the Collège de France, Paris. He joined Keele University in 2022 as a Lecturer in Physical Chemistry. The CreissenLab investigates electrolysis for the sustainable production of plastic precursors from  $CO_2$  and waste materials. Through catalyst design, integration, and investigation, we establish catalytic systems that can work at high rates of reaction with a range of devices (www.creissenlab.com)

#### **References**

14. A. Perazio, M. Schreiber, C. E. Creissen\*, M. Fontecave\*, ChemElectroChem, 2024, 11, e202400045

- 15. A. Perazio, C. E. Creissen\*, J. G. Rivera de la Cruz, M. Schreiber, M. Fontecave\*, ACS Energy Lett., 2023, 8, 2979-2985
- 16. L. S. Cousins, C. E. Creissen\*, Nanoscale, 2024, 16, 3195-3925
- 17. C. E. Creissen, J. G. Rivera de la Cruz, D. Karapinar, D. Taverna, M. Schreiber, M. Fontecave\*, Angew. Chem. Int. Ed., 2022, 61, e202206279

# Direct air carbon capture for solar chemicals synthesis

# **Sayan Kar**,<sup>\*1</sup> Dongseok Kim,<sup>1</sup> Ariffin Bin Mohamad Annuar,<sup>1</sup> Bidyut Bikash Sarma,<sup>1</sup> Michael Stanton,<sup>1</sup> Erwin Lam,<sup>1</sup> Subhajit Bhattacharjee,<sup>1</sup> Suvendu Karak,<sup>1</sup> Heather F Greer,<sup>1</sup> and Erwin Reisner<sup>\*1</sup>

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## Abstract

Direct air carbon capture (DACC) is an emerging technology that actively decreases atmospheric  $CO_2$  levels, but it is currently cost-intensive due to the need for  $CO_2$  desorption, transportation, and storage. A lucrative approach is to utilise the captured  $CO_2$  on-site to produce value-added renewable chemicals and close the carbon loop.<sup>1</sup> However, current  $CO_2$  utilisation technologies predominantly require concentrated  $CO_2$  feed that limits their overall integration with dilute stream  $CO_2$  capture processes.

We have developed a solar-powered direct air carbon capture and utilisation (DACCU) reactor that produces solar synthesis gas through on-site utilisation of air-captured CO<sub>2</sub> using sunlight. The reactor is envisioned to operate in a diurnal cycle, where CO<sub>2</sub> is selectively captured from the air during the night to produce CO<sub>2</sub>-free air (0 ppm CO<sub>2</sub>). Subsequently, the captured CO<sub>2</sub> is photochemically converted on the spot during the day using sunlight to produce renewable synthesis gas. Synthesis gas, which is a mixture of CO and H<sub>2</sub>, is an industrial building block that can be subsequently used for renewable fuel and complex chemical production. Combining state-of-the-art CO<sub>2</sub> capture and utilisation techniques, our solar DACCU technology offers an alternative to CO<sub>2</sub> transportation and storage following DACC, enabling on-site production of renewable chemicals in a circular fashion.

# **References**

18. Kar et al. Joule 2023, 7, 1496

# The effect of Zr on Bi electrocatalyst for enhancing CO<sub>2</sub> conversion to formic acid

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#### Abstract

The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) at low temperature has attracted tremendous interests for the potential to produce diverse value-added products. Among the producible products, formic acid (HCOOH) is one of the most commercially viable products from CO<sub>2</sub> electrolysis as it could be utilized for H<sub>2</sub> storage and transportation. Even though Bi catalysts have been focused with its high activity, CO<sub>2</sub> conversion does not still meet requirement for practical utilization. Meanwhile, local CO<sub>2</sub> concentration nearby electrode surface has been reported for significant effect on CO<sub>2</sub>RR activity<sup>1,2</sup>. As a strategy to increase available CO<sub>2</sub> reactant nearby catalysts, we have proposed Zr/Bi compound catalysts. In this presentation, Zr-MOF (UiO-66) with Bi has been presented to increase CO<sub>2</sub> conversion<sup>3</sup>. Then, we will discuss how the Zr compound affect the improvement of CO<sub>2</sub>RR with Zr/Bi compounds model catalyst.

For Zr-MOF synthesis, terephthalic acid and triethylamine were dissolved in dimethylformamide (DMF) at 120 °C. Then, Zr-MOF was synthesized by mixing with ZrCl<sub>4</sub>. Lastly, Bi was deposited on Zr-MOF by NaBH<sub>4</sub> reduction method. For Zr/Bi compound synthesis, bismuth chloride, zirconium chloride and Ketjen black (KB) were dissolved in aqua regia. Bi/Zr compound powder was collected by evaporating and treating with KOH solution. Then, it was calcined in hydrogen atmosphere. For electrochemical evaluation, cathode was fabricated on carbon paper by drop-casting or spray-coating with catalysts ink. Then, it was tested with flow-cell reactor for cyclic voltammetry (CV) and chronopotentiometry test under CO<sub>2</sub> flow. Reaction products were quantified by gas and liquid chromatography. Materials were characterized by XRD, SEM, TEM, Raman, FTIR, etc.

First, synthesized Bi/UiO-66 electrocatalysts show the 2.5 - 3.0 times higher current density than Bi only sample whereas Faradaic efficiencies of all synthesized samples for formic acid production are not significantly changed. It indicates only CO<sub>2</sub> conversion rate is increased by incorporating Zr-MOF structure. However, interestingly, various characterizations such as XRD, Raman, FTIR and XPS after CO<sub>2</sub> electrolysis revealed UiO-66 is structurally evolved forming carbonate-coordinated Zr-hydroxide suggesting Zr has an important role for promoting CO2 conversion. Then, we will discuss the role of Zr by establishing Zr/Bi compound catalysts. As shown in Fig. 1, Zr/Bi compound electrocatalysts also show the remarkably increased CO<sub>2</sub> reduction current density when it is compared with Bi only sample. Figure 2 shows the results of surface pH observed by in situ Raman spectroscopy. In case of Bi/Zr compound (B/Zr = 2), pH value is lower than Bi only probably due to high local CO<sub>2</sub> concentration. From these results, Zr has a crucial role to increase local CO<sub>2</sub> reactant nearby Bi electrocatalysts, promoting CO<sub>2</sub> conversion rate.



Fig. 1. I-V curves of synthesized Zr/Bi compounds for CO<sub>2</sub>





#### **References**

(1) M. R. Singh, Y. Kwon, Y. Lum, J. W. Ager, and A. T. Bell, J. Am. Chem. Soc. 2016, 138, 13006. (2) M. R. Singh, J. D. Goodpastera, A. Z. Webera, M. Head-Gordon, A. T. Bell, Proc. Proc. Natl. Acad. Sci. USA. 2017, 114, E8812.

# Investigating cation-dependent water oxidation kinetics on iridium based oxides

Yemin Tao,<sup>1</sup> Tomohiko Utsunomiya,<sup>2</sup> Haiting Yu,<sup>3</sup> Caiwu Liang,<sup>1</sup> Yifeng Wang,<sup>1</sup> Ifan E. L. Stephens,<sup>1</sup> Yu Katayama,<sup>2</sup> Aliaksandr S. Bandarenka,<sup>3</sup> James R. Durrant,<sup>4</sup> Mary P. Ryan,<sup>1</sup> Reshma R. Rao.<sup>\*1</sup>

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#### Abstract

Hydrogen is a clean and high-energy-density fuel, making it a key enabler of a sustainable energy future. Among available technologies, proton exchange membrane (PEM) electrolysers is a leading technology to produce hydrogen with zero carbon emissions. However, their widespread adoption is hindered by sluggish oxygen evolution reaction (OER) kinetics at the anode [1]. Iridium-based oxides are considered the most promising catalysts for OER. However, the nature of the interfacial water structure, and the influence of ions at the interface on the reaction kinetics, remains largely unknown. [2-3].

While most research focuses on catalytic materials, the role of the electrolyte in modulating OER activity is often underestimated. This study explores the influence of electrolyte cations (0.1 M MOH, M = Li, Na, K, TMA) on the OER performance of iridium-based catalysts. Our findings reveal that larger cations enhance OER activity, highlighting a critical connection between electrolyte composition and catalytic efficiency. Using laser-induced current transient technique, we examined the electric double-layer properties for each cation and determined the potential of maximum entropy (PME) [4]. These results were complemented by operando optical spectroscopy measurements that were used to determine the energetics of the active sites and their intrinsic kinetics for OER. These insights provide a holistic understanding of the electrified interface and demonstrate how electrolyte cations influence OER kinetics. This work offers valuable guidance for optimizing PEM electrolyser design to accelerate the transition toward green hydrogen production.

- 1. Bernt, M., & Gasteiger, H. A. (2016). Influence of ionomer content in IrO2/TiO2 electrodes on PEM water electrolyzer performance. *Journal of The Electrochemical Society*, 163(11), F3179.
- 2. M., Boettcher, S. W., & Caspary Toroker, M. (2017). Influence of electrolyte cations on Ni (Fe) OOH catalyzed oxygen evolution reaction. *Chemistry of Materials*, 29(11), 4761-4767.
- 3. Huang, B., Rao, R. R., & Shao-Horn, Y. (2021). Cation-dependent interfacial structures and kinetics for outersphere electron-transfer reactions. *The Journal of Physical Chemistry C*, 125(8), 4397-4411.
- 4. [4] Hou, S., Fischer, R. A. (2022). Dual in situ laser techniques underpin the role of cations in impacting electrocatalysts. *Angewandte Chemie*, 134(24), e202201610.

# Synergistic effect of multifold smart composite for the self-cleaning and energy-saving built environment

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# Abstract

Buildings account for over 40% of global carbon emissions due to energy consumption for heating, cooling, and lighting. Achieving the ambitious target of net-zero emissions by 2050 requires effective control of energy ingress and egress in the built environment.<sup>1</sup> To address the growing demand for energy-efficient and visually comfortable buildings, innovative high-performance smart glazing systems have been developed using advanced composite materials.<sup>2</sup> Solar energy chemicals play a critical role in these systems, offering thermal comfort while maintaining visual transparency and dynamic waterresistance properties, making them ideal for smart materials applications. This study introduces a multifunctional smart composite based on an optimized In<sub>2</sub>O<sub>3</sub>/ZnO-polymethyl methacrylate-paraffin blend. The composite is designed to reduce heat exchange through a self-cleaning, energy-saving envelope suitable for sustainable built environments (Figure 1). The developed coating integrates photosensitive metal oxides and phase change materials, demonstrating exceptional thermal comfort performance when applied as a glazed window. The composite exhibits temperature-dependent transparency, with a maximum transparency of 88% at 65 °C and a minimum of 68% at 22 °C. These transparent-to-translucent transitions are highly reproducible across 50 cycles.<sup>3</sup> In addition to tunable transparency, the composite offers switchable wettability, showing hydrophobic behavior at lower temperatures.<sup>3</sup> The performance of the composite glazing was evaluated through temperature profiling and ray optics simulation using the COMSOL Multiphysics numerical model. This research highlights the potential of such advanced materials to enhance building energy efficiency, providing a promising pathway for a sustainable and future-ready built environment.



**Figure 1**: A facile smart composite material demonstrating a synergistic effect on thermal comfort and self-cleaning properties, designed for a sustainable built environment.

# **References**

5. Commun Eng 3, 145 (2024). https://doi.org/10.1038/s44172-024-00291-4

- 6. <u>https://theconversation.com/smart-windows-could-be-the-next-big-thing-in-renewable-heating-245053</u> (Research Blog, The Conversation, A. Roy, 2024)
- 7. ACS Sustainable Chem. Eng. 10, 20, 6609–6621 (2022). <u>https://doi.org/10.1021/acssuschemeng.2c00260</u>

# Developing devices and characterisation tools for efficient and stable photoelectrochemical cells based on earth-abundant materials

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### Abstract

Photoelectrochemical cells (PECs) offer a potential pathway towards sustainable fuel production, for example through solar-powered water splitting into oxygen and hydrogen fuel. However, so far high solar-to-fuel generation efficiency (>15%) has only been demonstrated using expensive and scarce inorganic III-V semiconductor photoelectrodes. PECs based on next-generation solution processed semiconductors (e.g. metal-halide perovskites, organics, and metal oxides) are less resource intensive, enable more environmentally friendly fabrication methods and allow greater choice of material properties compared traditional inorganic technology. However, solution-processed PECs fall far short of the necessary combination of efficiency and stability for large-scale deployment.

Here, I will first present protected photoanodes based on organic semiconductor light absorbers and inorganic-carbon protection sheets that can achieve photocurrents (>25 mAcm<sup>-2</sup>) close to the theoretical limit for their bandgap (1.4 eV) at 1.23V vs RHE, and with multi-day stability under operating conditions. This was achieved by integrating a organic bulk-heterojunction with a graphite sheet functionalized with earth-abundant NiFeOOH water oxidation catalyst, which provides both water resistance and electrical connection between the catalyst and the photoactive layer without any losses. I will further demonstrate that when combined with a second, wide-band, organic semiconductor light absorber, tandem photoelectrochemical cells with unassisted (zero-bias) solar-to-hydrogen efficiency exceeding 5% could be fabricated, amongst the highest reported efficiency for photoelectrochemical devices based on non-toxic and earth-abundant materials. [1]

Secondly, I will present a new photoelectrochemical characterization tool, photo-electrochemical mass spectrometry (PEC-MS), that enables, for the first time, the real-time detection of multiple photoelectrochemical reaction products with pico.mol.s<sup>-1</sup> sensitivity. I will demonstrate how this tool can be used to gain novel insight into the photoelectrochemical and photocatalytic reaction and loss pathways in existing materials (hematite, bismuth vanadate), and aid the development of better photoelectrochemical and photocatalytic devices.



**Figure 1**: (a) Energy levels of a protected organic BHJ photoanode. (b) Shematic of photoelectrochemical mass spectrometry set-up (top) and measured oxygen evolution transient under illumination of a hemtatite photoanode.

## **Biography**



Flurin is a Lecturer in Green Energy and Sustainable Engineering at Queen Mary University of London. He obtained his PhD in 2018 from Imperial College London, for which he received the Technology Partnership Prize from the Department of Physics. Following his PhD, Flurin was awarded an EPSRC Doctoral Prize Fellowship to work on inorganic/organic bilayer solar cells and photodetectors and became an Assistant Supervisor in the Department of Physics. In 2023 he was awarded an Imperial College Research Fellowship to work on materials and devices for sustainable solar fuels generation, before moving to Queen Mary as a Lecturer in January 2024, where he is a leading a group on developing sustainable solutionprocessable semiconductors for solar energy conversion.

#### **References**

8. Dabozci\*, <u>Eisner\*</u>, Nelson\*, Eslava\* et al., Nature Energy, Just Accepted Manuscript. Pre-print available at <u>https://doi.org/10.26434/chemrxiv-2024-vshsx</u>.

# Light optimization methods for high rate photocatalysis

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## Abstract

Whole system approaches and understanding is necessary to facilitate our progression towards a sustainable energy network. Photocatalysis and electrocatalysis have widespread uses in various domains, including solar energy conversion, water purification, air purification, and the synthesis of organic compounds. The impact of photons, and specifically light intensity, is a key factor for photocatalytic technology and yet little research has focused on the optimisation of the incident sunlight matched with photocatalytic properties. This talk aims to provide an overview of the key design principles for solar concentrators specifically tailored for photocatalytic receivers. We will explore various aspects of the design process, including the selection of concentrator types, geometric considerations, material choices, tracking mechanisms, and optical efficiency enhancement techniques. By understanding and implementing these design principles we can develop higher rate photocatalysis systems run sustainably from solar energy.

# Photocatalysis with metallic nanoparticles

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### Abstract

Localized surface plasmons in metallic nanoparticles give rise to very strong light absorption. The decay of these excitations results in the generation of energetic or "hot" electrons and holes which can be harvested and harnessed for applications in photovoltaics, photocatalysis and light sensing. To optimize hot carrier production in devices, a detailed theoretical understanding of the relevant microscopic processes, including light-matter interactions, plasmon decay and hot electron thermalization, is needed. In my talk, I will describe a material-specific theory of hot-carrier generation and relaxation in metallic nanoparticles which combines a classical description of the electromagnetic radiation with large-scale atomistic quantum-mechanical simulations. I will present results for hot carrier distributions in spherical nanoparticles of gold, silver and copper and discuss the relative importance of interband and intraband transitions as function of nanoparticle size. Next, I will describe how CO<sub>2</sub> reduction performance of gold nanoparticles can be enhanced by changing the nanoparticle shape. Finally, I will present results for bimetallic Au-Pd photocatalysts and demonstrate a large enhancement in hydrogen production can be achieved in antenna-reactor architectures.

# Chalcogenide thin film photocathodes for photoelectrochemical hydrogen evolution

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## Abstract

Hydrogen fuel is a sustainable energy alternative to environmentally damaging fossil fuels. Photoelectrochemical hydrogen production is a green, low carbon method for generating hydrogen directly from solar energy. Photocathodes for hydrogen evolution reaction (HER) require the use of a p-type semiconductor with high absorption coefficient, optimal band edge alignment and appropriate band gap. Strong contenders for this are thin film chalcogenides such as Culn(S.Se)<sub>2</sub> (CISSe) and Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> (CZTSSe), p-type semiconductors who offer promise of simple, cheap and scalable solution-processability and low material usage.<sup>1</sup> In this work, solution-processed CZTSSe and CISSe with atomic layer deposition (ALD) surface modification layers are explored as photocathode materials for HER. To better understand the intrinsic activity of the chalcogenide material, it is initially studied without the addition of common efficiency boosting layers such as buffer layers or cocatalysts. Unfortunately, as is the case for many semiconductor materials, CZTSSe and CISSe are prone to surface degradation in direct contact with the electrolyte in the required potential windows. The solutionprocessing can also lead to homogeneity issues and pinholes on the absorber films surface, easily observed by electrochemical voltammetry in the presence of a redox couple. To overcome this, ultrathin ALD deposited AIO<sub>x</sub> protection layers and their effect on surface stability of the material are explored. ALD is an ideal technique for thin film surface modifications due to its highly controllable and reproducible deposition, both in terms of thickness and in terms of material stoichiometries and properties.<sup>3</sup> The insulating alumina provides an effective protection layer with thicknesses as low as 0.55 nm, yet there is a balance between stability and photocurrent density (and therefore efficiency). Electrochemical impedance spectroscopy was applied to understand the effect of increasing AlOx thickness on electron transfer to further understand this balance. This was found to be a universally applicable strategy, as improvements in efficiency and stability are observed with ALD protection layers even after the addition of buffer layers. The chalcogenides seem to suffer from high rates of recombination, which was improved greatly by addition of buffer layers. Photoelectrochemical measurements using single wavelength LEDs, both in the presence of redox electron scavengers and without, are carried out to better understand the activity of these chalcogenide absorber photoelectrode structures towards sustainable hydrogen production.

- 9. Liang, G. et al., Adv. Energy Mater. 2023, 13(19), 2300215.
- 10. Yoon, N. et al., Nanomaterials 2023, 13(8), 1361.
- 11. Pastukhova, N. et al., Adv. Mater. Interfaces 2021, 8, 2002100.
- 12. Ahmad, N. et al., Adv. Sci. 2023, 10, 2302869.

# Mechanistic insights to photo-physical processes and light-driven ionics in organic based semiconductors for efficient photocatalytic hydrogen evolution

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## Abstract

As our societies struggle to meet their ambitions for decreasing greenhouse gas emissions and the Paris Climate agreement, research into alternative solar energy conversion and storage technologies becomes even more relevant. Solar fuel production by photocatalysis is an economically promising route, especially when driven by earth abundant and organic materials. While organics' bottom-up design possibilities promise tailorable structure-function relationships for enhanced activity, the advancement is often hindered by limiting knowledge of interwoven photo-physical processes and properties that lead to recombination losses.[1]

In this talk, I will explain how time-resolved (transient) spectroscopy techniques in combination with varying environmental conditions can be used to provide insights into the very beginning of the solar energy conversion process chain, focusing on exciton generation and separation, and charge stabilization. This enables us to better understand light-matter interactions, and to tailor them to address bottlenecks associated with exciton recombination.

Our recent study on a series of functionalized polymers with varying porosity has revealed that not a maximization of a BET surface area is key, but rather the active interaction area with the photocatalytic environment, if exciton or charge separation is driven by sacrificial agents.[2]

In context of photocatalysis, interactions with aqueous ions, which are highly relevant for enabling applications in sea water conditions, are typically disregarded. Our study on suspended nanoparticles in presence of different salt shows how ions can impact stabilization of excitons and significantly extend their lifetimes, thereby enabling a new way to address excitons' commonly fast and rate-limiting recombination.[3]

Lastly, I will introduce Terahertz permittivity measurements as convenient technique to probe the complex permittivity, and with that the dielectric properties of organic semiconductors on ps-time scales. The dielectric response defines exciton binding and is hence relevant for charge carrier photogeneration in all solar energy conversion technologies, but its values are highly frequency dependent, and commonly extracted at timescales orders magnitude off the ps-regime. Our study focusing on carbon nitrides now reveals dielectric screening and transport properties at the early time scales of solar energy conversion process chains. At the same time, it shows that also in this ultrafast regime, the environment and ions can matter, and strongly enhance photophysical parameters.[4]

**Figure 1**: Left: Exemplary illustration of excitons in organic semiconductor (here, 2D ionic carbon nitride *K-PHI*) before they being separated to drive energy conversion function. Right: Environmentally affected dielectric properties that describe exciton binding and charge generation, focussing on the relevant ps-time scale in the THz regime [4].



- 13. T. Banerji, F. Podjaski, J. Kröger *et al.*: Polymer photocatalysts for solar-to-chemical energy conversion. *Nat. Rev. Mater.* 6, 168–190 (2021).
- B. Willner, C. M. Aichiston, F. Podjaski *et al.*: Correlation between the Molecular Properties of Semiconducting Polymers of Intrinsic Microporosity and Their Photocatalytic Hydrogen Production. *J. Am. Chem. Soc.* 146, 45, 30813–30823 (2024).
- 15. F. Podjaski, S. Gonzalez Carrero, C. Aichiston, P. Khlat, K. Steward, L. Hart, S. Hillman, J.-S. Kim, I. McCulloch, J. R. Durrant. *In preparation*.
- R. Jahangir, F. Podjaski, P. Alimard, S. A. J. Hillman, S. Davidson, S. Stoica, A. Kafizas, M. Naftaly, J. R. Durrant: Terahertz-permittivity of Carbon Nitrides: Revealing humidity-enhanced dielectric properties on the picosecond timescales relevant for charge carrier photogeneration. *Submitted.* <u>https://www.arxiv.org/abs/2411.06226</u>.

# Invited talk: Transition metal oxides: passivating layers, electrocatalysts, photoelectrodes?

# David J. Fermin

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## Abstract

Transition metal oxides (TMOs) are a vast family of compounds that have been investigated in a range of electrochemical energy conversion systems including, water electrolysis, photo(electro)chemical water splitting, transparent conducting layers, passivating coatings, fuel cells and metal-air batteries. Complex TMOs compounds involving more than two different cations (e.g., perovskites and pyrochlores) are often characterized by strong electron correlations, which manifest themselves by acute composition dependence of their opto-electronic properties. In the context of solar fuel, we could ask: what do make TMOs effective electrocatalysts, solar absorbers or even a passivation layers? There is a wealth of literature in which parameters such as oxide composition and electronic structure (as probed by DFT and photoemission spectroscopy) have been linked to their electrocatalytic and photoelectrochemical activity. These approaches often propose parameters such as d-orbital occupancy, oxygen binding energy, oxygen vacancies, covalency and metal oxidation state as so-called activity descriptors. In this contribution, we shall examine how the combination of electrochemical experiments and accurate electronic structure calculations are key for rationalizing the properties of complex TMOs.[1-6] In addition parameters such as electronic band gaps (which are often not directly accessible from optical measurements), I shall emphasize the notion of the position of d-orbitals in the electrochemical energy scale as a pivotal parameter for understanding the photoelectrochemical and electrocatalytic properties of these compounds.

## References:

- 1. Celorrio et al., ChemElectroChem, 2016, 3, 283
- 2. Celorrio, V. et al. ACS Catal. 2021, 11 (11), 6431
- 3. M. Alkhalifah et al., J. Am. Chem. Soc. 2022, 144, 4439
- 4. X. Sun et al. Adv. Energy Mater. 2020, 12, 2002784
- 5. X. Sun et al. Chem. Sci. 2022, 13, 11252
- 6. S. Gonzalez-Poggini, ACS Appl. Energy Mater. 2024, 7, 2622

## **Biography**



David J. Fermín (PhD, FRSC) is the Professor of Electrochemistry and Head of the Bristol Electrochemistry and Solar Team. He was born in Venezuela and studied Chemistry at the Universidad Simón Bolívar, where he initiated his research career investigating electronically conducting polymers under the supervision of Prof. Benjamin R. Scharifker. He completed his PhD on semiconductor photoelectrochemistry at the University Bath in 1997, moving to the Swiss Federal Institute Lausanne taking up a research position on solar energy conversion at molecular interfaces.

In 2001, he received the Tajima Prize by the International Society of Electrochemistry for his contributions to the field of photoelectrochemistry. In 2003, he obtained a Swiss National Science Foundation Professorial Fellowship joining the University of Berne, before moving to the University Bristol in 2007. At the University of Bristol, he coordinates research activities across the hydrogen value chain as well as novel technologies for photovoltaic solar cells. He is a Net Zero academic lead for the University of Bristol and Impact Director for the School of Chemistry.

# Spectroscopic measurements of quasi-Fermi level splitting in Fe<sub>2</sub>O<sub>3</sub>

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## Abstract

Quasi-Fermi level splitting (QFLS) occurs in semiconductors under light irradiation, generating an internal voltage. In the case of photoanodes for photoelectrochemical (PEC) water splitting, this internal voltage helps drive the surface redox chemistry. It has been shown that, for slow redox processes such as water oxidation, the QFLS differs from the external photovoltage often reported as the change in open circuit potential (OCP).<sup>1</sup> As a result, direct measurements of the QFLS from PEC measurements alone is challenging. Several strategies have been reported in the literature for measuring QFLS, including vibrating Kelvin probe surface photovoltage measurements<sup>1</sup> and surface potential measurements from a dual working electrode setup<sup>2</sup>.

Recently, we demonstrated that pump-probe spectroscopy can be used to measure the QFLS of metal oxides (e.g. BiVO<sub>4</sub>) under operando conditions by directly probing hole populations.<sup>3</sup> For systems where water oxidation proceeds via the same mechanism under PEC and electrochemical conditions, the QFLS can be measured by taking the difference in applied potential required to achieve the same steady state hole population in the light and the dark. Building on this, in this work we investigate QFLS as a function of light intensity and explore its relationship with the photovoltage derived from currentvoltage curves, employing  $Fe_2O_3$  as a model system.

Our spectroscopy data show that the prepared Fe<sub>2</sub>O<sub>3</sub> films demonstrate ideal behaviour as the hole guasi-Fermi level (EF,p) approaches the valence band edge (VBE). For this material, the QFLS measured from spectroscopy strongly correlates with the photovoltage measured from the currentvoltage curves, providing easy access to the QFLS for this system. The absolute value of the QFLS is highly dependent on the external applied bias and is limited by the position of the bulk Fermi level relative to the VBE. The measured QFLS differs from the change in OCP under illumination, highlighting the importance of the electrochemical QFLS to photoanode performance.

- 17. S. Daemi, A. Kundmann, K. Becker, P. Cendula & F. E. Osterloh, Energy Environ. Sci., 2023, 16, 4530–4538.
- 18. R. Chen, D, Zhang, Z. Wang, D. Li, L. Zhang, X. Wang, F. Fan & C. Li, J. Am. Chem. Soc. 2023, 145, 4667-4674.
- 19. B. Li, L. I. Oldham, L. Tian, G. Zhou, S. Selim, L. Steier and J. R. Durrant, J. Am. Chem. Soc., 2024, 146, 12324-12328.

# Cation-enhanced nitrogen reduction studies with a photoelectrochemical p-InP-CoMo system

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## Abstract

Photoelectrochemical systems afford the benefits of electrochemistry coupled with the ability to employ direct solar energy to drive chemical reactions on photoelectrode surfaces. The direct PEC systems allow tuneability of electron density at the electrocatalyst surface through optimising the photon flux reaching the electrode surface, and lowers the overvoltage required to drive reactions by supplying photogenerated carriers for the redox processes.

Successful deposition of CoMo alloys on InP were previously reported by us with promising initial indications of nitrogen fixation from XPS analysis of the Mo 3*p*/ N 1*s* region.<sup>1,2</sup> Since, we have explored the potential of these systems towards ammonia synthesis as well as investigating the relative influences of the different components of a photoelectrochemical system on the final performance of the p-InP-CoMo system towards NRR. Extensive control experiments were conducted through measurements under OCP conditions, light vs dark, and with and without supplying N<sub>2</sub> to the system.

In-depth testing of the electrodes towards nitrogen reduction to ammonia alongside an extensive range of control experiments were carried out in a plain 50 mM  $H_2SO_4$  solution, as well as with addition of  $Cs_2SO_4$ , and  $K_2SO_4$  salts. The Cs > K > no salt trend was observed with the electrodes, as widely reported in the literature for  $CO_2RR$  and OER studies.<sup>3–5</sup> This study highlights the important role that electrolyte enhancement can play alongside the effects of photoillumination, applied overvoltage, and  $N_2$  supply that bring a photoelectrochemical system to life.

- 1. M. Kaur, M. Walker, S. Hindmarsh, C. Bolt, S. York, Y. Han, M. R. Lees and K. Brinkert, *Faraday Discuss.*, 2023, **243**, 354–377.
- 2. C. J. H. Jacobsen, S. Dahl, B. S. Clausen, S. Bahn, A. Logadottir and J. K. Nørskov, *J. Am. Chem. Soc.*, 2001, **123**, 8404–8405.
- 3. H. Khani, A. R. Puente Santiago and T. He, *Angew. Chem.*, 2023, **135**, e202306103.
- 4. D. Park and Y. Jung, *Chem Catal.*, 2024, **4**, 100823.
- 5. Y.-C. Hao, Y. Guo, L.-W. Chen, M. Shu, X.-Y. Wang, T.-A. Bu, W.-Y. Gao, N. Zhang, X. Su, X. Feng, J.-W. Zhou, B. Wang, C.-W. Hu, A.-X. Yin, R. Si, Y.-W. Zhang and C.-H. Yan, *Nat. Catal.*, 2019, **2**, 448–456.

# A carbon cathode for lithium mediated electrochemical ammonia synthesis

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## Abstract

Lithium-mediated electrochemical nitrogen reduction to produce ammonia has been brought to the forefront of sustainable nitrogen reduction recently since it has been the only method to withstand rigorous protocols.<sup>(1)</sup> In recent years, vast improvements have been made towards the selectivity and efficiency of the system by altering the composition of the electrolyte<sup>(2, 3)</sup> or by utilising a gas diffusion electrode.<sup>(4)</sup> The working electrode has been scarcely researched and thus far has been metal electrodes such as stainless steel<sup>(4)</sup> or copper<sup>(5)</sup>. Here, we have employed carbon as the cathode in a flow cell which introduces tuneability and high surface area. We have screened various current densities and ethanol concentrations (the proton carrier) to achieve an increased Faradaic efficiency. This will open avenues to now tune the properties of carbon electrodes in order to tailor them for the reaction's requirements for example by increasing the heteroatom content to increase the lithiophilicity of the carbon.

## <u>References</u>

- Andersen, S. Z.; Čolić, V.; Yang, S.; Schwalbe, J. A.; Nielander, A. C.; McEnaney, J. M.; Enemark-Rasmussen, K.; Baker, J. G.; Singh, A. R.; Rohr, B. A.; Statt, M. J.; Blair, S. J.; Mezzavilla, S.; Kibsgaard, J.; Vesborg, P. C. K.; Cargnello, M.; Bent, S. F.; Jaramillo, T. F.; Stephens, I. E. L.; Nørskov, J. K.; Chorkendorff, I., Nature, 2019, 570 (7762), 504–508. https://doi.org/10.1038/s41586-019-1260-x.
- (2) Du, H.-L., Matuszek, K., Hodgetts, R., Dinh, K., Cherepanov, P., Bakker, J. M., MacFarlane, D., & Simonov, A. N., The chemistry of proton carriers in high-performance lithium mediated ammonia electrosynthesis. Energy & Environmental Science, 2023. <u>https://doi.org/10.1039/D2EE03901J</u>
- (3) Westhead, O., Spry, M., Bagger, A., Shen, Z., Yadegari, H., Favero, S., Tort, R., Titirici, M., Ryan, M. P., Jervis, R., Katayama, Y., Aguadero, A., Regoutz, A., Grimaud, A., & Stephens, I. E. L., Journal of Materials Chemistry A, 2023, <u>https://doi.org/10.1039/D2TA07686A</u>
- (4) X. Fu, J. B. Pedersen, Y. Zhou, M. Saccoccio, S. Li, R. Sažinas, K. Li, S. Z. Andersen, A. Xu, N. H. Deissler, J. Bjarke, V. Mygind, C. Wei, J. Kibsgaard, P. C. K. Vesborg, J. K. Nørskov and I. Chorkendorff, Science, 2023, 379, 707–712.
- (5) Li, K., Shapel, S. G., Hochfilzer, D., Pedersen, J. B., Krempl, K., Andersen, S. Z., Sažinas, R., Saccoccio, M., Li, S., Chakraborty, D., Kibsgaard, J., Vesborg, P. C. K., Nørskov, J. K., & Chorkendorff, I., ACS Energy Letters, 2022, 7(1), 36–41. <u>https://doi.org/10.1021/acsenergylett.1c02104</u>

# Approaches to enhance hematite performance for photoelectrocatalytic water oxidation

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## Abstract

Photoelectrochemical (PEC) water splitting represents a sustainable and cost-effective route to convert solar energy directly into chemical energy in the form of molecular hydrogen. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has been targeted as one of the most promising metal oxide photoanodes in PEC configuration due to its natural abundance, effective use of visible light and excellent photo and chemical stability. However, hematite photoanodes still underperform in terms of solar-to-hydrogen efficiency, far below its corresponding theoretical value. The sluggish four-electron-transfer water oxidation reaction is one of the main reasons for the lower efficiency of hematite photoanodes. To facilitate the water oxidation



**Figure 1. (a)** LSV of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/sIr under dark and illumination at visible light of 480 nm in 0.1 M KNO<sub>3</sub> solution with a pH of 7.0 (left) and butler plots (right). **(b)** Proposed mechanism and optimised structures of the reaction intermediates of the oxygen evolution reaction on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (110)(left), on the Fe site of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/sIr (110) (middle), and on the Ir site of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/sIr (110) (right).

surface process, modification of hematite via decoration cocatalysts has been proposed as а promising strategy to lower the reaction barrier. One of the efficient most electrocatalyst for oxidation water is iridium.

Here, I present our work on single-atom iridium on hematite (α-Fe<sub>2</sub>O<sub>3</sub>/slr) and evaluate their role as catalytic site for photoelectrocatalytic oxidation water The reaction. α-Fe<sub>2</sub>O<sub>3</sub>/sIr delivered a onset potential low (Figure 2a. determined by butler plots, Figure 2a right) of~0.82 V vs RHE, which cathodically shifted 0.44 V with respect to bare q-

Fe<sub>2</sub>O<sub>3</sub>, as well as a significantly improved photocurrent value, particularly at lower potentials. This was related to the faster hole transfer exhibited by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/sIr, demonstrated by in situ transient absorption spectroscopy. Density functional theory calculations revealed the mechanism for water oxidation using sIr as a catalytic centre to be the preferred pathway as it displayed a lower onset potential than the Fe sites (Figure 2b).

Our energy band structure calculations showed that sIr induces mid-gap states with Ir 4d orbitals, which could serve as hole traps, facilitating the hole transfer from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to sIr followed by fast water oxidation. The reaction on the sIr site has a significantly lower energy barrier(1.01 eV) than when Fe acts as the active site (1.80 eV). These results provide for the first time a deeper understanding of the interplay between the electronic structure, hole transfer, and depletion in water oxidation mechanisms.

If time allows it, I will also summarise additional approaches to promote hematite photoactivity my research group has been exploring over the last few months.

## **Biography**



Ana Sobrido graduated in Chemistry in Canary Islands in 2004. She obtained her Ph.D. in Materials Science from the Materials Science Institute of Barcelona and the Autonomous University of Barcelona in 2009. After some time in industry, she returned to academia in 2011, taking up a postdoctoral position at University College London investigating new graphitic carbon nitrides for energy applications. In 2016, she was offered an Academic Fellow position at QMUL that led to a Lecturer position in 2019. Since 2022 Ana is a UKRI Future Leaders Fellow, and since 2023, a Professor of Sustainable Energy Materials. Her research focuses on designing materials for energy conversion and storage, including oxygen electrocatalysts, flow battery electrodes and photoanodes for water oxidation.

#### References

 Q. Guo, Q. Zhao, R. Crespo-Otero, D. Di Tommasso, J. Tang, S. Dimitrov, M. M. Titirici, X. Li, A. Jorge Sobrido, Single-atom iridium on hematite photoanodes for solar water splitting: catalyst or spectator? *JACS*, 2023, 145, 1686-1695.

# Design strategies for reducing charge recombination in polymer photocatalysts and photoelectrodes

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## Abstract

High performance, light absorbing semiconductors are of intense interest for the solar-driven generation of sustainable fuels in photocatalytic and photoelectrochemical systems. Whilst metal oxides are the most-studied photoactive materials for reactions such as hydrogen evolution from water, organic semiconductors can advantageously be synthesised from abundant sources; offer control over microstructure, light harvesting properties and redox potentials; and have the potential to be used in technologically simple devices.

In this talk, I will primarily use transient absorption spectroscopy to demonstrate that generating charges which can live for microseconds and beyond is critical to the performance of a variety of different polymer photocatalyst and photoelectrode systems 1–4. However, generating large yields of these long-lived charges is a serious challenge in organic materials as excitons and charges can recombine through multiple mechanisms on timescales ranging from picoseconds to seconds. In this talk I will present several design strategies for retarding geminate and non-geminate recombination mechanisms, with particular focus on the timescales at which sacrificial agents and water influence the photophysics of the polymer system.

I will first demonstrate that picosecond hole transfer to the sacrificial donor TEA competes strongly with exciton recombination in a series of sulfone-containing polymer photocatalysts2. Whilst beneficial for preventing recombination, the dependence of the long-lived electron yield on the polymers' ability to oxidise TEA highlights that researchers need to be wary of unknowingly optimising unsustainable scavenger reactions.

Alternatively, excitons can be separated using an organic heterojunction. However, whilst a PM6:Y6 heterojunction can efficiently separate excitons on the picosecond timescale with no applied bias – as in a photocatalytic system – non-geminate charge recombination prevents long-lived charges from accumulating unless spatially separated by an applied bias3. I will demonstrate that the yield and lifetime of PM6 hole polarons can be improved in a PM6:Y6 photoanode by adding a planar PM6 overlayer on top of the bulk heterojunction which prevents bimolecular recombination through spatial separation.

Finally, I will show that the inclusion of oligo(ethylene glycol) side chains to a polymer photocatalyst extends the lifetime and yield of the active electrons relative to its alkylated analogue4. In this case, the hydrophilicity of the side chains causes substantial swelling, with the resulting spatial separation again reducing bimolecular recombination on the microsecond timescale. Overall, I aim to show that recombination can be reduced in a wide range of photo(electro)chemical organic materials through several different design strategies.

## **References**

1. Sachs, M. et al. Understanding structure-activity relationships in linear polymer photocatalysts for hydrogen evolution. Nat. Commun. 9, 4968 (2018).

 Hillman, S. A. J. et al. Why do sulfone-containing polymer photocatalysts work so well for sacrificial hydrogen evolution from water? J. Am. Chem. Soc. 144, 42, 19382–19395 (2022).
Lee, T. H., Hillman, S. A. J. et al. J. R. Long-Lived Charges in Y6:PM6 Bulk-Heterojunction Photoanodes with a Polymer Overlayer Improve Photoelectrocatalytic Performance. Adv. Energy Mater. 2300400 (2023).

4. Woods, D. J., Hillman, S. A. J. et al. Side-chain tuning in conjugated polymer photocatalysts for improved hydrogen production from water. Energy Environ. Sci. 13, 1843–1855 (2020).

# Revolutionizing solar efficiency: Al-driven performance assessment of amorphous thin film solar cells with non-transparent and transparent front electrodes

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## Abstract

Thin film technology has become a widely adopted technique for applying various materials onto different substrates. Within the field of solar cell technology, thin film technology signifies a new generation of solar cells, which have the potential to substitute costly monocrystalline semiconductors with more affordable materials like amorphous silicon. However, the incorporation of silver as a front contact plays a crucial role in the cost assessment of thin film solar cells. As a result, we are actively investigating alternatives to silver that can serve as effective front contacts. To facilitate this exploration, we have created a theoretical model to assess the viability of copper and Aluminum Zinc Oxide (AZO) as substitutes for silver, comparing their performance against a simulated ideal ohmic contact. This model has enabled us to generate energy band diagrams and current-voltage (J-V) characteristic curves for a detailed comparison. Additionally, we have examined the effects of utilizing non-transparent contacts in comparison to transparent conductive oxides like AZO. Our results reveal a 27% decrease in current when AZO is used instead of the traditional silver front contact. This finding highlights the potential of AZO as an efficient and economical alternative to silver, presenting encouraging opportunities for the advancement of thin film solar cell technology.

# Impact of cobalt intercalation on the electrochemical properties of layered birnessite under water oxidation potentials

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#### Abstract

Green hydrogen produced through water electrolysis is set to decarbonise major polluting chemical synthesis industries. However, water splitting is significantly hindered by inefficiencies during the oxygen evolution reaction at the electrolyser anode. Overcoming these challenges currently requires the use of expensive electrocatalysts derived from scarce precious metals.<sup>1</sup> Understanding the inherent electrochemical energy storage mechanisms of energy materials is essential if they are to fulfil their predicted role of facilitating the transition to net zero emissions. Although layered manganese oxides such as birnessite (δ-MnO<sub>2</sub>) have been extensively explored as battery cathode and supercapacitor materials,<sup>2</sup> their application towards alkaline water oxidation has been relatively uncharted due to their poor intrinsic activity but could still be promising candidates if modified. In this work we intercalate cobalt ions between the manganese oxide layers of hydrous birnessite films to tune and modulate their electronic properties, resulting in improved activity and stability. Combining spectroelectrochemical techniques such as operando X-ray absorption and UV-vis amongst others has revealed an interesting coupling in redox activity between manganese and cobalt centres with applied potential. These results suggest that some degree of optimal synergistic interaction between the intercalated cation and birnessite host, mediated through interlayer confined water, can govern the switch between capacitive charge storage and electrocatalytic capability.<sup>3</sup> Further elucidating the phenomena at these complex electrode-electrolyte interfaces could lead to the design of highly tailorable, resilient and more sustainable energy materials.

- 21. Lagadec and Grimaud. Nat. Mater. 2020, 19 (11), 1140-1150.
- 22. Liu and Higgins. Nat. Catal. 2024, 7 (5), 469-471.
- 23. Boyd et al. Nat. Mater. 2021, 20 (12), 1689–1694.

# Poster titles

#	Name	Institute	Poster title
1	Zhongqing Shen	Newcastle University	Solar-driven plastic waste to valuable chemicals
2	Romain Tort	Imperial College London	Nitrogen reduction to ammonia: Species activities unify selectivity trends
3	Ava Blandford	University of Bristol	Exploring photoelectrochemical properties of buried Culn(S,Se) <sub>2</sub> junctions prepared by solution based methods
4	Josh Buckingham	University of Bath	Field effected aerosol assisted chemical vapour deposition (FE-AACVD) of thin film materials
5	Max Court	Queen Mary University of London	Ferroelectric – photocatalyst nanocomposites for enhanced solar fuel generation
6	Charlie Brown	University of Bath	Aerosol-assisted chemical vapour deposition of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> , BiFeO <sub>3</sub> , and BiVO <sub>4</sub> as effective photoanodes for photoelectrochemical water splitting
7	Meimei Yang	Imperial College London	Probing conductivity changes of the supports for iridium oxide water oxidation catalysts in- situ with the interdigitated electrodes
8	Yifeng Wang	Imperial College London	Investigating the role of oxide species in Ni- based catalysts for alkaline water electrolysers
9	Karen Ai	Imperial College London	Charge dynamics behind photocatalytic and photovoltaic performance of polymer/non- fullerene acceptor bulk heterojunction
10	Cathal Burns	Northumbria University	Microbial photohybrids for semi-artificial photosynthesis
11	George Creasey	Imperial College London	Up-scaling photoelectrochemical reactors – from lab-scale optimisation to outdoor field testing
12	Suvendu Karak	University of Cambridge	Scalable photocatalyst sheets for semi- artificial solar reforming
13	Lewis Cousins	Keele University	Molecular electrocatalyst development for efficient CO <sub>2</sub> valorisation
14	Kanyapat Plub-in	Imperial College London	Electrochemical oxidation of glycerol on platinum electrode
15	Teng Fei	Imperial College London	Electron dynamics in Ru hybrid photocatalysts with conjugated polymer P10 for CO <sub>2</sub> reduction

16	Shijie Yu	Imperial College London	Temperature dependent studies on the dynamic behaviour of hematite photoanodes for photoelectrochemical water splitting
17	Caiwu Liang	Imperial College London	Key role of oxidising species for water oxidation on iridium oxides revealed by time- resolved optical and X-ray spectroscopies.
18	Santiago Rodríguez- Jiménez	University of Cambridge	A simple strategy to adapt gas fermenting bacteria for light-driven CO₂ valorization through domino catalysis
19	Hsin-Yu Chen	University of Liverpool	Enhanced C <sub>2</sub> <sup>+</sup> selectivity and stability in CO <sub>2</sub> electroreduction using five-fold twinned copper nanowires
20	Hanzhi Ye	Imperial College London	Electrochemical glycerol oxidation towards lactic acid production over multi-component catalysts
21	Hansaem Jang	University of Liverpool	Enabling the electroreduction of carbon dioxide on gold by cationic surfactants