

First UK Solar Chemicals Network Symposium

Liverpool, 11th and 12th January 2024

TALK ABSTRACTS

Thursday 11th January

Session 1 – Biocatalysts

Invited Talk - Professor Stephen Wallace, University of Edinburgh

"Phototrophic Bacteria for Biocompatible Alkene Hydrogenation"

Hydrogenation is one of the most ubiquitous reactions in the modern chemical industry and industrial H_2 is predominantly derived from diminishing fossil resources. Concurrently, the use of metabolically engineered microorganisms has emerged as an elegant approach to sustainable chemical synthesis, where native and/or *de novo* biosynthetic pathways can be assembled in living cells to enable the production of chemical target molecules directly from renewable feedstocks via fermentation. In my talk I will present our recent work on the use of microorganisms to generate $H_{2(g)}$ from glucose, and how these living cells can be combined with a biocompatible membrane bound Pd catalyst for alkene hydrogenation. This will include the first use of a phototrophic bacterium to generate high pressures of bio- H_2 from organic acids and light, demonstrating the use of photo-fermentation to enable sustainable H_2 production for chemical synthesis. Overall, this research demonstrates how organic chemistry can be combined with microbiology and synthetic biology to create hetero- and photo-trophic living cells for the *in situ* delivery of synthetic reagents from renewable feedstocks.

C Megarity, University of Manchester 'Multi-enzyme Cascades Jam-packed and Electrified'

Multi-enzyme cascades are typically not amenable to direct electrochemical control. By exploiting the crowded nanoconfinement of enzymes in a porous electrode, and a key enzyme in photosynthesis called ferredoxin NADP⁺ reductase (FNR), a new platform called the Electrochemical Leaf (e-Leaf) now enables multi-enzyme pathways to be electrochemically driven and controlled.

Some discoveries made possible by this electrified nanoconfinement will be outlined.

(i) Deracemisation, achieved by control of the electrode potential which allowed us to simultaneously drive a co-entrapped pair of alcohol dehydrogenases with opposing enantioselectivities in oxidation, and then reduction, to convert a racemic alcohol -> ketone -> a single alcohol enantiomer.

(ii) An extended five-enzyme cascade driven reversibly with *in situ* production of CO_2 a substrate for one of the enzymes.

(iii) Evidence that the crowded pore environment facilitates the breakdown of an inactive enzymeintermediate complex by efficient sequestering of the inhibitory intermediate tightly bound to the key player in a four-enzyme cascade in which two cofactors, NADPH and ATP, are confocally recycled.

- 1. B. Cheng, R. S. Heath, N. J. Turner, F. A. Armstrong and C. F. Megarity*, Chemical Communications, 2022, 58, 11713-11716.
- 2. G. Morello, C. F. Megarity and F. A. Armstrong*, Nature Communications, 2021, 12, 340.



3. C. F. Megarity*, T. R. I. Weald, R. S. Heath, N. J. Turner and F. A. Armstrong*, ACS Catalysis, 2022, 12, 8811-8821.

M Kuhnel, University of Hoheneim

'Solvent engineering as a tool to enable oxygen-tolerant solar chemicals production with air-sensitive enzymes'

Natural enzymes are among the most efficient electrocatalysts for solar fuel production with hydrogenases and carbon monoxide dehydrogenases capable of reversibly catalysing H⁺-to-H₂ (HER) and CO₂-to-CO (CO₂RR) conversion, respectively, at minimal overpotentials and high current densities. However, their inhibition by oxygen, which is inevitably generated during water splitting, limits the usefulness of these enzymes.

Here, we present a novel approach to making these enzymes oxygen tolerant beyond the established concepts of encapsulation or genetic engineering. Instead, we use the solvent to act as a simple yet effective dynamic oxygen shield. We show that deep eutectic solvents (DESs), a low-cost and non-toxic type of ionic liquids can be tailored to impede O_2 diffusion and that hindered O_2 diffusion allows HER to outcompete O_2 inhibition. With this approach, the residual photocatalytic HER activity of [NiFeSe] hydrogenase/TiO₂ under a constant air purge increases from ~4% in water to ~90% in DES (relative to the activity under N₂). Electrochemical measurements further demonstrate that this concept is equally applicable to enabling O_2 -tolerant CO_2RR at carbon monoxide dehydrogenase immobilised on a carbon-nanotube electrode.

References

M.G. Allan, T. Pichon, J.A. McCune, C. Cavazza, A. Le Goff, M.F. Kühnel, "Augmenting the Performance of Hydrogenase for Aerobic Photocatalytic Hydrogen Evolution via Solvent Tuning", *Angew. Chem. Int. Ed.* **2023**, *62*, e202219176

M.G. Allan, M.J. McKee, F. Marken and M.F. Kuehnel, "Solvent-controlled O₂ diffusion enables air-tolerant solar hydrogen generation", *Energy Environ. Sci.* **2021**, *14*, 5523–5529



Session 2 – Advanced Electrocatalysis

Invited Talk – Dr Reshma Rao, Imperial College London

'Operando characterisation of electrochemical interfaces'

The efficiency, lifetime and resilience of emerging electrochemical technologies for green energy conversion and storage, chemical synthesis, and pollution control relies on atomiclevel processes occurring at complex catalytic interfaces. Therefore, we need experimental probes that can shed light on the underlying physical and chemical processes occurring at these dynamic electrochemical interfaces, at the nanometer scale, to enable rational design of catalysts.

In this talk, I will demonstrate how advanced surface characterisation techniques such as optical spectroscopy and X-ray absorption spectroscopy can be used to investigate electrochemical processes relevant for green fuel and chemical production, on interfaces with varying degrees of complexity, from model surfaces to industrially relevant systems. Particularly, I will illustrate how we can identify and quantify the density of potential-dependent intermediates, the degree of interaction between them, and the intrinsic rate of reaction. In addition to determining the changes in the catalyst, I will also show how the nature of interfacial electrolyte can be probed using surface enhanced infrared absorption spectroscopy. Using such mechanistic insight, I will demonstrate how we can develop design rules for discovering next-generation catalysts.

H Jang, University of Liverpool

'Cationic surfactant switches on the carbon dioxide reduction reaction at gold surfaces'

Occurrence of electrochemical carbon dioxide reduction is intimately associated with the species present at the outer Helmholtz plane. Charged ionic species such as metal and organic cations at the electrical double layer are reported to electrostatically stabilize adsorbed carbon dioxide intermediates, thereby activating the electroreduction into carbon monoxide at gold surfaces. Here we show that the electroconversion can also be enabled in the presence of cationic cetrimonium surfactant with a hydrophobic tail group. The cetrimonium-assisted production of carbon monoxide, albeit chromatographically quantifiable, is not detected through an electrochemical CO-stripping method or an infrared spectroscopic method under operando conditions. The findings suggest that cetrimonium facilitates the removal of produced carbon monoxide from the electrode surface, disabling the electroanalytical observation of those molecules. In addition, surface-enhanced infrared adsorption spectroscopy results indicate that the difficulty in CO detection stems from the orientation of cetrimonium ions at the surfaces at potentials negative of the potential at the point of zero charge of gold electrode.

C Tseng, Imperial College London

Probing the Effects of Doped Iridium Oxide on Oxygen Evolution Reaction Using Operando Spectroelectrochemical Techniques

Growing concerns about emissions, fossil fuel sustainability, and geopolitics underscore the rising need for affordable renewable fuels. Hydrogen generation through water splitting using proton exchange membrane (PEM) electrolysers is a promising solution, but the reliance on scarce and expensive iridium oxide for oxygen evolution is a challenge. Research suggests incorporating non-precious metal oxides in iridium oxide catalysts can enhance performance while reducing costs.^{1,2}

In this project, we investigate a series of mixed titanium-iridium oxides and test them against pure iridium oxide electrocatalysts. We use rotating disk electrode to test their electrochemical activity and



stability, followed by operando UV-Vis absorption spectroscopy to probe and quantify the populations of surface species and track the kinetics of different redox species generated during oxygen evolution reaction. The combination of these two techniques provides a holistic picture of reactions occurring at the electrode-electrolyte interface of iridium oxides that is otherwise very challenging to probe. We believe this study will serve as a steppingstone for future designs of more cost-efficient PEM electrolysers.

- 1. Oh, Hyung-Suk, et al. "Electrochemical catalyst–support effects and their stabilizing role for IrO x nanoparticle catalysts during the oxygen evolution reaction." *Journal of the American Chemical Society* 138.38 (2016): 12552-12563.
- 2. Zheng, Ya-Rong, et al. "Monitoring oxygen production on mass-selected iridium-tantalum oxide electrocatalysts." *Nature Energy* 7.1 (2022): 55-64.



Session 3 – Light Harvesting

Invited Speaker – Professor Tomas Edvinsson, Newcastle University/Uppsala University *Pathway to utilize IR photons for efficient solar fuel generation*

About half of the energy in the solar spectrum resides in the infrared (IR) region and results in a mismatch between the solar energy distribution and the energetic requirements for the water splitting reaction leading to a fundamental efficiency problem for a single band gap device. While tandem approaches demonstrate high efficiencies at elevated cost, Z-schemes, photon up-conversion, and intermediate band gap photovoltaics are still in developmental stages and hindered by low conversion efficiencies. Here we highlight that utilization of serial interconnected photo-absorber with a buried junction approach [1,2] is an alternative and cost-effective solution to the spectral mismatch problem. Taking losses due to charge carrier separation and overpotential for catalysis into account, the maximum solar-to-hydrogen (STH) efficiency for a series interconnected solar splitting device is 24.6 %, compared to 32.0 % for an optimum double junction tandem device. [3] Applying modified Cu-In-Ga-Se₂ (CIGS) within the approach allows harvesting of photons up to 1200 nm in the solar spectrum and convert this energy into solar fuel beyond 10% STH efficiency. [1,4] The approach also allow construction of scalable and thermally-integrated solar water splitting modules with up to 13.4 % STH efficiency. [5] We will also outline how operando Raman spectroscopy can be utilized to unveil electrocatalyst reformulations into the active catalyst phase [6,7] and their structural integrity. [8]

1. Jacobsson, T. J., Fjällström, V., Sahlberg, M., Edoff, M., Edvinsson, T. Energy & Environmental Science, 2013, 6, 3676. 2. Jacobsson, T. J., Fjällström, V., M., Edoff, M., Edvinsson, T. Energy & Environmental Science, 2014, 7, 2056. 3. Jacobsson, T. J., Fjällström, V., M., Edoff, M., Edvinsson, T. Solar Energy Materials & Solar Cells, 2015, 138, 85. 4. Pehlivan, I. B., Atak, G., Niklasson, G.A., Stolt, L., Edoff, M., Edvinsson, T. Nano Energy, 2021, 81, 105620. 5. Pehlivan, I.B., Sagui, N.A., Oscarsson, J., Qiu, Z., Zwaygardt, W., Lee, M., Mueller, M., Haas, S., Stolt, L., Edoff, M., Edvinsson, T. J. Mater. Chem. A, 2022, 10, 12079. 6. Qiu, Z., Tai, C.-W., Niklasson. G.A., Edvinsson, T. Energy & Environmental Science, 2019, 12, 572. 7. Qiu, Z., Ma, Y., Edvinsson, T. Nano Energy, 2019, 66, 104118. 8. Dürr, R.N., Maltoni, P., Tian, H., Jousselme, B., Hammarström, L., Edvinsson, T. ACS Nano 2020, 15, 13504.

Y Liu, University of Cambridge

'Semiconductor-enzyme hybrids for solar chemical synthesis'

Converting solar energy into clean chemical fuels using H₂O and CO₂ 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.^[1]

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,^[2] CulnGaS₂,^[3,4] ZnFe₂O₄,^[5] CuFe₂O₄,^[6] α -Fe₂O₃,^[7,8] and LaFeO₃^[9] have been explored for direct solar H₂ production and CO₂ 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.

References

- 1. Y. Liu, S. Webb, P. Moreno-García, A. Kulkarni, P. Maroni, P. Broekmann, R. D. Milton. *JACS Au*, 2023, 3 (1), 124-130.
- 2. Y. Liu, C. Pulignani, S. Webb, S. J. Cobb, S. Rodríguez-Jiménez, D. Kim, R. D. Milton, E. Reisner. Submitted. ChemRxiv: <u>https://doi.org/10.26434/chemrxiv-2023-zksp5</u>
- 3. 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.
- 4. 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.
- 5. Y. Liu, M. Xia, L. Yao, M. Mensi, D. Ren, M. Grätzel, K. Sivula, N. Guijarro. *Adv. Funct. Mater.*, 2021, *31* (16), 2010081.
- 6. Y. Liu, F. Le Formal, F. Boudoire, L. Yao, K. Sivula, N. Guijarro. *J. Mater. Chem. A*, 2019, 7 (4), 1669–1677.
- 7. Y. Liu, N. Guijarro, K. Sivula. *Helvetica Chimica Acta*, 2020, *103* (6), e2000064.
- 8. Y. Liu, F. Le Formal, F. Boudoire, N. Guijarro. ACS Appl. Energy Mater., 2019, 2, 6825–6833.
- 9. 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.

D Benetti, Imperial College London

'Photoactivation: manipulating the charge dynamics of metal oxides photoelectrodes with light'

To fully exploit the potential of photoelectrochemical water splitting (PEC), it is necessary to develop photoanodes that efficiently absorb sunlight and drive the kinetically demanding oxygen evolution reaction (OER). Among the numerous light absorber candidates, metal oxides (MOx) possess attractive properties such as low-cost processing, earth abundance, and better stability in aqueous media compared to other semiconductor materials. However, despite intensive research over the past decade, conversion efficiencies for these materials are still low. To overcome this obstacle, it is essential to fully understand the dynamic charge processes that occur in MOx during the water-splitting reaction.

This work focuses on investigating n-type MOx, such as BiVO4. It has been observed that changes in the electrolyte and extended light exposure (referred to as the photoactivation process) markedly affect the kinetics of the oxygen evolution reaction (OER). Utilizing advanced in-operando spectroscopy methods, we will explore how these modifications impact the charge dynamics and correlate them with any surface or bulk modification.



Thursday 12th January

Session 4

Invited Speaker – Professor Camille Petit, Imperial College London "Gas phase CO2 photoreduction using porous materials"

Reshaping our energy portfolio considering the sustainability of global energy resources is central to the European Energy Roadmap 2050. Hence, researchers need to identify efficient routes towards solar fuels production. Unlike H2 evolution, CO2 photoreduction has been less studied. Given the scope for CO2 utilisation in a carbon-constrained future, there is an exciting opportunity to devote targeted research towards CO2 photoreduction. Photocatalysis is one route towards CO2 reduction. Yet, the design of a cost-effective, sustainable, efficient and robust photocatalyst remains a highly challenging task.

Historically, the majority of studies on CO2 reduction photocatalyst have predominantly focused on crystalline and non-porous materials, with TiO2 remaining the 40-year old benchmark in the field. Yet, porous materials can present interesting photocatalytic features. The high surface area allows one to favour access to catalytic sites, tune the strength of adsorption/desorption of reactants/products and possibly control electronic transfer mechanisms. In the case of amorphous porous materials, scaling up can be easier than for crystalline materials.

Herein, we will discuss our recent work towards the development of CO2 photoreduction catalysts that present a porous and sometimes an amorphous character. We will highlight in particular our studies on boron nitride, hypercrosslinked polymers, and metal organic frameworks. For all types, we show that the selective conversion of CO2 into CO is possible under both UV and visible light. Using analytical and spectroscopic tools, we are starting to understand the mechanisms of reaction of these materials.

S Kar, University of Cambridge

'Integrated Capture and Solar-driven Utilization of CO2 from Flue Gas and Air into Syngas'

It is becoming likely that a net carbon-zero future will rely on the recycling of atmospheric CO_2 to produce sustainable fuels and chemicals. However, most current CO_2 solar-utilization processes depend on pure and pressurized CO_2 as the reactant, whose production from air is expensive. Thus, the integration of carbon capture with solar utilization technologies is urgently needed for developing processes for a future net-zero economy.

Here we report an integrated CO₂ capture and photoelectrochemical (PEC) utilization reactor that captures CO₂ from dilute streams and directly converts it into synthesis using sunlight as the sole energy input. The reactor operates by combining captured CO₂-to-fuel reduction at a photocathode with selective oxidation of waste plastic-derived ethylene glycol to glycolic acid at the anode. CO₂ is captured in an amine or hydroxide solution, and the subsequent PEC conversion occurs in a triple cation perovskite-based photocathode with an immobilized molecular Co-phthalocyanine complex as captured CO₂ reduction catalyst. A bimetallic alloy anode completes the circuit by catalyzing EG oxidation. The overall process uses flue gas/air as a carbon source, discarded plastic waste as an electron donor, and sunlight as the sole energy input, opening avenues for future carbon-neutral/negative solar fuel and waste upcycling technologies.

M Daboczi, Imperial College London

'Halide perovskite and organic semiconductor photoelectrodes for stable water oxidation and unassisted solar water splitting'



Session 5

S Yao, Imperial College London

'Spectroscopic Investigation of Long-lived Electrons in Titanium-Based Metal-Organic Frameworks for Hydrogen Evolution in Dark Photocatalysis'

Metal-organic frameworks (MOFs) have emerged as promising candidates for photocatalysis due to their unique structures and versatile properties. It was recently demonstrated that the titanium-based MOFs, MIP-177-LT (Ti), shows promising chemical stability ¹ and photoactivity towards formic acid oxidation to produce hydrogen ². In this study, we use transient photoinduced absorption spectroscopy to measure charge carrier dynamics on the femtoseconds-seconds timescale. We find that MIP-177-LT (Ti) exhibits a remarkable ability to generate stable accumulated electrons by UV and visible illumination without the need for hole scavengers. A significant population of photogenerated electrons persists for more than 48 hours and is accompanied by a colour change from white to black. Remarkably, this colour change is fully reversable on exposure to electron scavengers O2 or methyl viologen, indicating the long-lived charges are still highly redox active. Efficient time delayed H₂ generation is observed after 30 min of 365 nm illumination and subsequent addition of Pt in the condition of dark photocatalysis, evolving 300 µmol/g H₂ within 30 min. The fact that MIP-177-LT (Ti) can generate a large yield of photoinduced long-lived electrons with high reactivity renders it highly promising for photocatalytic applications, and for studies involving photo-charging properties.

References

- 1. Nat Commun 9, 1660 (2018).
- 2. Energy Environ. Sci., 2023,16, 167-177

J Alvim, Imperial College London

'Investigation of structural instability of Cu2WO4 photocathode during CO2 reduction reaction'

Photoelectrochemical (PEC) CO₂ reduction reaction (CO₂RR) is a sustainable route to produce valueadded chemicals using solar energy, water, and CO₂ as the inputs. Although significant progress has been made in developing semiconductors to promote PEC-CO₂RR, efficiency of scalable materials remains insufficient for commercial application.¹ The little-studied p-type semiconductor Cu₂WO₄ has suitable properties to be used as a photocathode for PEC-CO₂RR, such as narrow band-gap (1.98 eV) and enhanced stability in comparison to Cu₂O binary oxide although it still not enough for practical application.² The reasons for the Cu₂WO₄ instability under CO₂RR conditions is still unclear and should be investigated to provide strategies for increasing the long-term stability of Cu₂WO₄ electrodes for solar fuel production. This work reports the performance of gas diffusion electrodes (GDE) based on Cu₂WO₄ as well as the investigation of photocorrosion mechanism of copper(I) tungstate during the PEC-CO₂RR. The CO₂ conversion into ethanol promoted by GDE/Cu₂WO₄ can be related to the structural stability of semiconductor. Moreover, *in situ* Raman spectroscopy measurements and X-ray Diffraction (XRD) analyses of Cu₂WO₄ photoelectrode corroborated with ICP-OES and XPS analyses, which suggest Cu₂O crystalline phase as product from Cu₂WO₄ degradation during the PEC-CO₂RR.

- 1. Wang, Q., Liu, J., Li, Q. & Yang, J. Stability of Photocathode: A Review on the Principle, Design and Strategies. *ChemSusChem* (2023).
- 2. Tayar Galante, M. *et al.* Arc Synthesis, Crystal Structure, and Photoelectrochemistry of Copper(I) Tungstate. ACS Appl Mater Interfaces 13, 32865–32875 (2021).



C Li, University of Liverpool

'Interplay of D/A twist angle and aggregation (π - π interaction) in controlling the nature of CT state formation'

Organic molecular materials have shown great potential in the field of photocatalysis. Controlling the aggregation of organic units offers a way to tune photocatalytic activity, but to achieve this we need to understand the underlying mechanisms occurring. Here we study solvent dependence of photophysical properties of a donor-acceptor molecule and how aggregation controls the charge transfer state that is an active photocatalyst by using time-resolved infrared and transient absorption spectroscopies.

E McQueen, University of Strathclyde

'Quantitative photocatalytic conversion of CO_2 to highly concentrated formic acid using a hybrid photocatalyst consisting of a conjugated polymer and a supramolecular complex'

Photocatalysts enable the conversion of CO2 to useful products such as formic acid, carbon monoxide and methane using visible light. However, most photocatalysts to date are limited by insufficient long-term durability and slow CO2 conversion rates. By assembling a hybrid photocatalyst1 consisting of a conjugated polymer semiconductor and a binuclear ruthenium(II)-ruthenium(II) supramolecular complex, a very active and durable photocatalytic CO2 conversion to formic acid was achieved, with a turnover number of 349,000 (one-order higher than the previously reported most durable hybrid photocatalyst)2, a turnover frequency of 6.5 s-1 (surpassing that of CO2 fixation by RuBisCO in natural photosynthesis, ~3 s 1)3, and an apparent quantum yield of 9.2% at 460 nm (the highest amongst hybrid photocatalysts reported to date). Remarkably, quantitative conversion of CO2 to formic acid was achieved at standard temperature and pressure. Further replenishment of the system with CO2 produced a very high concentration of formic acid up to 0.40 M (at which 1 litre is equivalent to 9.9 litres of H2). This development enables the green generation of formic acid as a potential hydrogen energy carrier produced directly by photocatalytic CO2 conversion.

- 1. Nakada, A.; Kumagai, H.; Robert, M.; Ishitani, O.; Maeda, K. *Acc. Mater. Res.* **2021**, *2* (6), 458–470.
- 2. Sakakibara, N.; Shizuno, M.; Kanazawa, T.; Kato, K.; Yamakata, A.; Nozawa, S.; Ito, T.; Terashima, K.; Maeda, K.; Tamaki, Y.; Ishitani, O. *ACS Appl. Mater. Interfaces* **2023**, *15* (10), 13205–13218.
- (John Andrews, T.; Whitney, S. M. Archives of Biochemistry and Biophysics 2003, 414 (2), 159– 169.



Session 6

O Thwaites, University of Liverpool

'Unravelling the Roles of Integral Polypeptides in Excitation Energy Transfer of Photosynthetic RC-LH1 Supercomplexes'

Understanding the photosynthetic processes occurring within the reaction centre-light-harvesting 1 (RC-LH1) supercomplexes of purple bacteria is crucial for uncovering the assembly and functional mechanisms of natural photosynthetic systems and underpinning the development of artificial photosynthesis. In this presentation, I examine the excitation energy transfer of various RC-LH1 supercomplexes of *Rhodobacter sphaeroides* via transient absorption spectroscopy, coupled with lifetime density analysis, and study the roles of the integral transmembrane polypeptides, PufX and PufY, in energy transfer within the RC-LH1 supercomplex. The results show that the absence of PufX increases both the LH1 \rightarrow RC excitation energy transfer lifetime and distribution due to the role of PufX in defining the interaction and orientation of the RC within the LH1 ring. While the absence of PufY leads to the conformational shift of several LH1 subunits toward the RC, it does not result in a marked change in the excitation energy transfer lifetime. [1, 2]

References

- Owen Thwaites, Bern M. Christianson, Alexander J. Cowan, Frank Jaeckel, Lu-Ning Liu, and Adrian M. Gardner. Unravelling the Roles of Integral Polypeptides in Excitation Energy Transfer of Photosynthetic RC-LH1 Supercomplexes. The Journal of Physical Chemistry B, August 2023.
- Peng Cao, Laura Bracun, Atsushi Yamagata, Bern M. Christianson, Tatsuki Negami, Baohua Zou, Tohru Terada, Daniel P. Canniffe, Mikako Shirouzu, Mei Li, and Luning Liu. Structural basis for the assembly and quinone transport mechanisms of the dimeric photosynthetic RC – LH1 supercomplex. Nature Communications, 13(1):1–12, 2022.

T Li, University of Manchester

'Sustainable Electrosynthesis of Cyclohexanone Oxime through Nitrate Reduction on a Zn-Cu Alloy Catalyst'

Cyclohexanone oxime is an important precursor for Nylon-6 and is typically synthesized via the nucleophilic addition-elimination of hydroxylamine with cyclohexanone. Current technologies for hydroxylamine production are, however, not environment-friendly due to the requirement of harsh reaction conditions. Here we report an electrochemical method for the one-pot synthesis of cyclohexanone oxime under ambient conditions with aqueous nitrate as the nitrogen source. A series of Zn-Cu alloy catalysts are developed to drive the electrochemical reduction of nitrate, where the hydroxylamine intermediate formed in the electroreduction process can undergo a chemical reaction with the cyclohexanone present in the electrolyte to produce the corresponding oxime. The best performance is achieved on a Zn₉₃Cu₇ electrocatalyst with a 97% yield and a 27% Faradaic efficiency for cyclohexanone oxime at 100 mA/cm². By analyzing the catalytic activities/selectivities of the different Zn-Cu alloys and conducting mechanistic studies via *in-situ* Raman spectroscopy and theoretical calculations, we demonstrate that the adsorption of nitrogen species plays a central role on catalytic performance. Overall, this work provides an attractive strategy to build the C–N bond in oxime and drive sustainable organic synthesis through electrochemical nitrate reduction, while highlighting the importance of controlling surface adsorption for product selectivity in electrosynthesis.

Reference

Jonathan Sharp, Anna Ciotti, Shaktis Waran, Max García-Melchor, Tengfei Li*. Sustainable Electrosynthesis of Cyclohexanone Oxime through Nitrate Reduction on a Zn-Cu Alloy Catalyst. ACS *Catal.* 2023, under review.

F Podjaski, Imperial College London

'Photophysics of gIDTBT nanoparticles in presence of aqueous salt ions and impacts on photocatalysis'



Broadly absorbing polymer nanoparticles (NP) are increasingly used as photocatalysts for (sacrificial) hydrogen evolution. Their increasing efficiencies are related to good absorption of visible light, and efficient as well as long-lasting charge generation in single materials as well as heterojunctions, since exciton lifetimes are typically limiting.¹ Substitution of alkyl side chains by glycol groups is known to enhance wettability and permittivity, and has recently been shown to also increase the yield of charge generation in neat gIDTBT NPs and heterojunctions made thereof, going in hand with high photocatalytic efficiency.^{1.2}

A largely unchartered research area however is the influence of sea water ions such as NaCl on the performance of such materials. We have studied their influence on the photocatalytic activity and photophysical properties of gIDTBT NPs by means of ultrafast transient spectroscopy and photoluminescence (PL) spectroscopy. These concentration and salt species dependent studies revealed an increasingly strong modification of intrinsically very short exciton lifetimes, and related modifications in PL properties for different cations. We will discuss the interwoven effects such ions can induce and put them in context to photocatalysis.

References

- 1. J. Kosco et al., Adv. Mater. 2022, 34, 2105007.
- 2. J. Kosco et al., Nat. Energy 2022, 7, 340-351.

P Sharma, University College London

'Catalysts for selective electrochemical conversion of CO₂ to methanol'

Carbon capture and utilization (CCU) present a promising pathway for mitigating climate change. CCU offers the two-fold advantages of mitigating atmospheric CO_2 levels and supplying valuable chemicals and fuels. Electrochemical CO_2 reduction (e CO_2R) emerges as a promising method for directly generating fuels and chemicals from CO_2 and water waste. In the current project, we aim to selectivity convert CO_2 to methanol electrochemically at ambient temperature and pressure conditions.

Methanol, being a liquid in ambient conditions, can be stored for long term. It is a very attractive substitute of the gasoline in transportation sector. Methanol can be used in transport sector by minor modifications of the engine, and it can use the existing fuels infrastructure¹. Moreover, it can even be directly utilized in fuel cells. Cooper is the most investigated catalyst for eCO₂R. eCO₂R on Cu tends to favour the production of multi-carbon products². The nanostructuring and alloying to create diverse interfaces offers a potential avenue for developing materials with enhanced catalytic activity and selectivity towards methanol³.

In this work, we systematically investigate Cu-Se and CuNCN materials for CO_2 reduction in a flow reactor for their eCO_2R performance. The results from materials development, electrochemical performance and different eCO_2R products selectivity will be presented.

References

- 1. J. Garza, A. T. Bell, M. Head-Gordon, ACS Catal, 8 (2018) 1490–1499.
- 2. G. A. Olah, Angew Chem Int Ed, 44 (2005), 2636-2639.
- 3. Yanrong Liu 1, Fangfang Li 1, Xiangping Zhang 2 3 4, Xiaoyan Ji, Current Opin Green Sustain Chem, 23 (2020), 10-17.

Acknowledgment: We acknowledges the Department for Energy Security and Net Zero (Project ID: NEXTCCUS) and the ACT program (Accelerating CCS Technologies, Horizon2020 Project No. 691712) for the financial support of the NEXTCCUS project (project ID: 327327).



Number	Name	Poster Title
		Catalysts for selective electrochemical conversion of CO ₂ to
1	P Sharma	methanol
		Ultrafast Electron Transfer from CuInS ₂ Quantum Dots to a
		Molecular Catalyst for Hydrogen Production: Challenging Diffusion
2	AJ Bagnall	Limitations
		Taking Inspiration from the Natural Carboxysome to Utilise
3	S Cobb	Atmospheric Concentrations of CO ₂
		Bipolar membrane electrolyzers for CO ₂ reduction using molecular
4	B Siritanarakul	catalysts
		Photophysics of gIDTBT nanoparticles in presence of aqueous salt
5	F Podjaski	ions and impacts on photocatalysis
	•	Photocatalytic Reforming of Diols over Pt/TiO ₂ for the Production
6	L Roebuck	of H ₂ and Value-Added Chemicals
		Unassisted (Photo)-electrochemical Water Splitting Using Multi-
7	S Saravanabavan	Junction Solar Cells in Microgravity
		Stabilized states (shallow traps) created by glycol sidechain on
8	T Fei	Polymer Photocatalyst FgBT extending charges lifetime
		Probing the Effects of Doped Iridium Oxide on Oxygen Evolution
9	C Tseng	Reaction Using Operando Spectroelectrochemical Techniques
		Halide perovskite and organic semiconductor photoelectrodes for
10	M Daboczi	stable water oxidation and unassisted solar water splitting
11	N Lin	
11	Y Liu	Semiconductor–enzyme hybrids for solar chemical synthesis
12	J Yang	Photonic band gap engineering of SnO ₂
		Iridium doped Antimony Tin Oxide as a stable material for the
13	A Malik	Oxygen Evolution Reaction in acid
	A Mohamad	Hybrid photothermal-photocatalyst sheets for solar-driven overall
14	Annuar	water splitting coupled to water purification
		Towards Pairing Solar Chemical Production with Central
15	A Sutton-Cook	Metabolism of S. oneidensis MR-1
		Organic semiconductor-BiVO ₄ tandems for solar-driven H ₂ O and
16	CWS Yeung	CO ₂ splitting
		Development of Hybrid Perovskite as Visible Light Photocatalyst for
17	H Wang	Solar Fuel Production
	Santiago Rodriguez	
18	Jimenez	Valorisation of CO ₂ and other abundant waste streams
19	J Wang	Photonic band gap engineering of SnO ₂
	0.10.10	Investigating charge carrier dynamics of metal oxide photoanodes
20	L Oldham	for photoelectrochemical water splitting
		Biomass photoreforming mediated by Ni(II) modified Bi ₂ WO ₆ and
21	LL Nascimento	Nb ₂ O ₅ photocatalysts
		Efficient Cu ₂ O Photocathodes for Aqueous Photoelectrochemical
22	M Xia	CO ₂ Reduction to Formate and Syngas
		Towards High-throughput Functional Materials Discovery for H ₂ O ₂
23	Y Li	Photoproduction
24	R Tort	Searching for the Rules of Electrochemical Nitrogen Fixation
25	H Ullah	Computational Modeling of Energy Materials



26	Q He	Develop new organic photoactive materials for solar energy conversion and photodetection
27	ТНе	Charge dynamics study in the effect of facet-engineering to BiVO ₄ photocatalysts systems
28	E Sokalu	Investigating the platinisation of p-type indium phosphide and the effect of precursor cations on surface morphology