Bath Monash Global PhD Programme in Sustainable & Circular Technologies

Project Title:	New Platforms for Photoelectrochemical Water Splitting
Supervisors at Bath: Supervisors at Monash:	Dr Andrew L. Johnson and Prof. Frank Marken Dr Cameron Bentley, Prof. Jie Zhang, and Dr Noel Duffy (CSIRO)
Home Institution (Bath):	Bath (Department of Chemistry)
Indicative period at Host Institution (Monash):	2.5 years (Bath) and 1.0 year (Monash): (2y:1y:0.5y)

Project Summary (to include a brief description of the relevance to sustainable & circular technologies)

Over thirty years ago, hydrogen was identified as "a critical and indispensable element of a decarbonised, sustainable energy system" to provide secure, cost-effective and non-polluting energy.[1] However, there is no naturally occurring H_2 source on earth, and it must be obtained through energy-intensive processes such as the electrolysis of water. Indeed, electrolytic water splitting is one of the most effective and environmentally friendly techniques for large-scale hydrogen production. It consists of two reactions of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) at the cathode and anode, respectively. While platinum group metals and iridium/ruthenium-based materials continue to be important catalysts for the HER and OER, respectively, their high cost and scarcity are one of the main obstacles for commercial production. Therefore, much effort has been directed to searching for active and efficient HER and OER oxide catalysts containing low cost, earth abundant constituents such as Cu Ti, Ni, Fe, W and Mo.[1]

A basic Photoelectrochemical Cell (PEC) device comprises of a semiconducting photoelectrode, a semiconducting or metallic counter electrode, and electrolyte (Fig. 1). In the case of a semiconducting photoanode, the photoanode absorbs light which has energy greater than or equal to the band gap energy of the semiconductor and generates an electron-hole pair which participate in the HER and OER respectively, thus completing the full water-splitting (*i.e.* water electrolysis) chemical reaction. The simplicity in design and the direct conversion of sunlight to hydrogen gas, a promising alternative to fossil fuel, make PEC an attractive choice for renewable energy research. However, there exist some non-trivial challenges in developing and enhancing PEC devices: (i) In reality, it is very challenging to obtain photoanode and photocathode materials with suitable bandgaps and matchable band edge positions for efficient spontaneous PEC water splitting. The restrictions on the viable semiconductor materials, resulting in the need for new stable OER materials with appropriate bad gags, protective overlay coatings as well as effective co-catalyst nanoparticles. (ii) Surface area and morphology of an electrocatalyst is a crucial feature that can significantly affect its practical performance. Nano-structuring (e.g., through the formation of nanosheets, nanorods, nanowires (Fig 1), and nanospheres) is a well-known strategy to increase the catalyst surface area, increasing the number of active sites and improving performance. However, not only the "quantity" but also the "quality" (e.g., intrinsic activity) of surface-active sites is highly crucial for determining catalytic performance.

Tuning the elemental composition is a key strategy to improve the "quality" of catalytic surface-active sites. For this reason, mixed metal oxides (MMOs) have been identified as excellent candidates for practical water splitting. Compared with their conventional single-element counterparts, MMOs feature multi-element (*i.e.* bi-metal and tri-metal) and undercoordinated active centres, which can be beneficial to the adsorption–desorption of intermediates, charge transfer, and durability.

Atomic layer deposition (ALD), uniquely amongst processes for thin film deposition, offers a mechanism by which both MMOs such as $NiCo_2O_4$, $NiFe_2O_4$, $CoFe_2O_4$, $BiVO_4$ and $BiFeO_3$ can be formed, as well as offering a low energy methodology for the fabrication of 3D conformal coatings. ALD relies on alternating, self-limiting reactions between gaseous reactants and an exposed solid surface to deposit highly conformal coatings, with a film thickness controlled at the sub-monolayer level. These advantages have rendered ALD a mainstream technique in microelectronics and have triggered growing interest in ALD for a variety of nanotechnology applications, including energy technologies.

In this project, we wish to tackle the development of new OER and HER materials in tandem, optimizing material efficiency, matching band gap of materials and maximizing the catalytic surface area. We will build on an already strong relationship between Monash and Bath,[2] using our proof-of-concept experiments as a basis for our ongoing work, screening our established precursor systems for the development of next generation MMO-based water splitting materials, such as $Ni_xFe_yO_4$.

The project is divided into (A) a materials production part focusing on selected aspects of precursor development for specific elements, as well as the synthesis, growth of ALD layer coatings, changing thickness and nano-crystal size, exploring different p- and n-type materials. Introducing post deposition treatments such as vacuum annealing we hope to control defect densities and improve materials performance. The second part of the project (B) will involve the electrochemical characterization with photo-electrochemical methods in Bath, and (C) photocatalysis and electrocatalysis studies with advanced spatiotemporal electrochemical techniques at Monash. Specifically, in part (C), the cutting-edge methods of Fourier Transformed alternating current voltammetry (FTac voltammetry) and scanning electrochemical cell microscopy (SECCM) will used for the *in situ* identification/characterisation of photo-catalytic active sites in *time* and *space*, respectively focusing on structure-activity relationships.[3] In the latter stages of the project focus will be directed towards use the facility available at CSIRO for scale up applications or our bast is show materials and architectures.

The relevance to sustainability and circular technologies is based not only on the development of materials for the evolution of hydrogen (and oxygen) as a viable renewable energy resource but also in the use of light to produce these products. While the initial aim of the work will be directed towards hydrogen production from acidic or alkaline solution, longer term goals include the use of sea water (in a clean photo-driven process) for H_2 and O_2 production. If successful later stages of the work will address additional targets such as carbon dioxide reduction in sea water.

1: Y. Zhu, Q. Lan Y. Zhong, H. A. Tahini, Z. Shao and H. Wang, *Energy Environ. Sci.*, 2020,**13**, 3361-3392

2: T. R. Harris-Lee, A. L. Johnson, L. Wang, P. J. Fletcher, J. Zhang, C. Bentley, C. R. Bowen and F. Marken, *New J. Chem.*, 2022,46, 8385-8392; T. R. Harris-Lee, J. Zhang, C. R. Bowen, P. J. Fletcher, Y. Zhao, Z Guo, J. W. F. Innocent, A. L. Johnson and F. Marken, *Electrocatalysis* 2021, 12, 12, 65–77; J. W. F. Innocent, M. Napari, A. L. Johnson, T. R. Harris-Lee, M. Regue, I. Sajavaara, J. L. MacManus-Driscoll, F. Marken and F. Alkhalil, Mater. Adv. 2021, 2, 273-279.

3: S. X. Guo, C. L. Bentley, M. Kang, A. M. Bond, P. R. Unwin, J. Zhang, Advanced Spatiotemporal Voltammetric Techniques for Kinetic Analysis and Active Site Determination in the Electrochemical Reduction of CO_2. *Acc Chem Res* **2022,** *55* (3), 241-251.

Features of the programme

- PhD researchers will be registered at both institutions and will be awarded a joint PhD degree.
- PhD researchers will be jointly supervised by academics from both Monash and Bath Universities.
- All PhD researchers in the joint programme will also undertake a bespoke advanced training plan covering a range of topics focusing on sustainability.
- Applicants can apply to either Monash University or the University of Bath as their nominated home institution.
- PhD researchers will undertake a period of no less than 12 months at the partner institution.
- Up to four scholarships/studentships will be offered. Additional and suitably qualified applicants who can access a scholarship/studentship from other sources will be also considered. Evidence of funding must be provided.
- The scholarships/studentships include:
  - a *full tuition fee sponsorship* provided by Monash or Bath for the course duration (up to a maximum 42 months). Note, however, that studentships for Bath-based projects will provide cover for UK/EU tuition fees ONLY.
  - *a living allowance (stipend)* provided by Monash or Bath Universities.

Note: Overseas Student Health Cover (OSHC) must be paid by the student, unless covered by the university.

How to apply

You MUST express interest for three projects in order of preference. Please submit your application at the Home institution of your preferred project ('Home' institution details can be found in the project summary). However, please note that you are applying for a joint PhD programme and applications will be processed as such.

The deadline to submit applications is 30th January 2023

Monash University

Expressions of interest (EoI) can be lodged through https://www.monash.edu/science/bath-monash-program. The EoI should provide the following information:

CV including details of citizenship, your Official Academic Transcripts, key to grades/grading scale of your transcripts, evidence of English language proficiency (IELTS or TOEFL, for full requirements see: https://www.monash.edu/graduate-research/faqs-and-resources/content/chapter-two/2-2), and two referees and contact details (optional). You must provide a link to these documents in Section 8 using Google Drive (Instructions in Section 8).

University of Bath

Please submit your application through the following link: https://www.csct.ac.uk/bath-monash-global-phd-programme/

Please make sure to mention in the "finance" section of your application that you are applying for funding through the joint Bath/Monash PhD programme for your specified projects.

In the "research interests" section of your application, please name the three projects you are interested in and rank them in order of preference. Please also include the names of the Bath lead supervisors.