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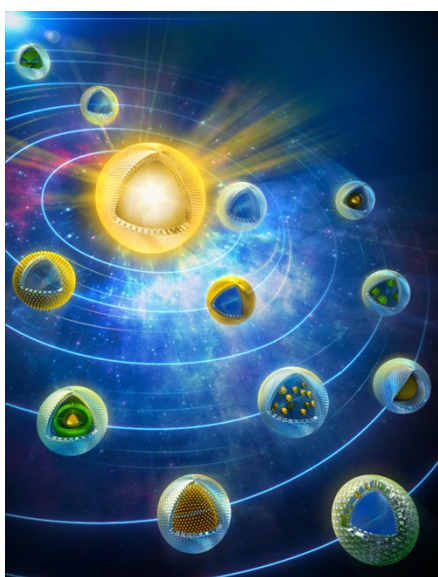
Biannual Research Report
November 2018 - March 2019



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Cover image



A schematic illustration of hollow catalytic devices with different structural configurations.

Image by Prof. Hua Chun Zeng's research group, IRP1.

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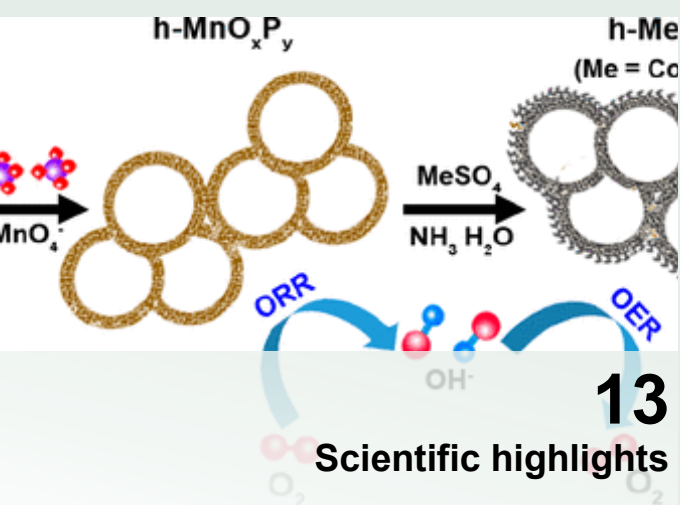
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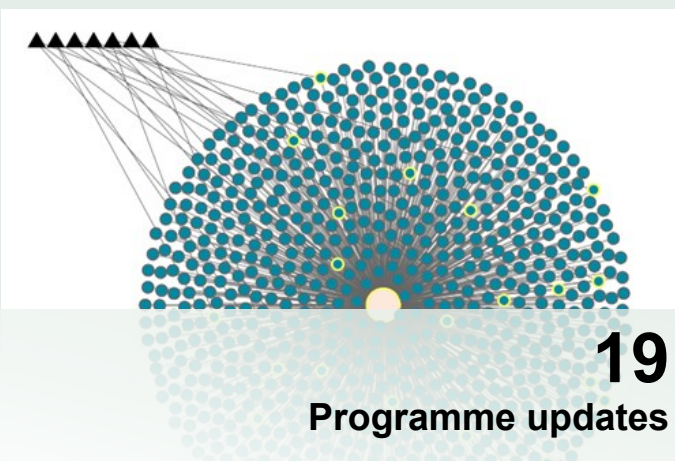
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FOREWORD

I am very pleased to present the 10th Biannual Research Report of the Cambridge Centre for Advanced Research and Education in Singapore (Cambridge CARES). This publication marks the beginning of Research Phase 2 for our flagship programme Cambridge Centre for Carbon Reduction in Chemical Technology (C4T). As well as the latest C4T research, this report contains an update on the progress of our first Intra-CREATE programme, eCO₂EP. There are also several articles on some of the practical impacts of our work, which I hope you will enjoy.

C4T PHASE 2

We had a smooth transition from Phase 1 to Phase 2 in November last year, continuing with the majority of our Phase 1 research areas and welcoming three new Interdisciplinary Research Programmes (IRPs). IRP Better Business looks at how we can best integrate and apply our research to industry here in Singapore and there is a new, separate IRP for the J-Park Simulator (part of IRP3 in Phase 1). The new Phase 2 IRP4 is on waste heat utilisation, with a focus on Singapore's marine industry. Our Principal Investigators from Singapore and Cambridge joined us in December for a Phase 2 kick-off meeting. This was a valuable opportunity for everyone to meet and plan the first few months of Phase 2.

INTRA-CREATE

Members of Cambridge CARES' first Intra-CREATE programme, eCO₂EP, met in Singapore for a workshop and progress meeting in March. One year in, the team is making good progress on their deliverables and have published further pa-

pers. You may find their update on page 87. We will soon commence a new Intra-CREATE programme between CARES and NUS, with the title 'An intelligent platform for efficient energy management in an eco-industrial park'.

HIGHLIGHTS

We were very glad to welcome our esteemed Scientific Advisory Committee to Singapore in March 2019 to present our first few months of progress in C4T Phase 2. The Committee enjoyed their visit and hearing about our latest research, and we look forward to hosting them again in 2020 for our Mid-Term Review.

WORKING WITH INDUSTRY

During the Scientific Advisory Committee visit, we hosted guests from local industry and government for an evening of C4T research presentations and networking. As we enter Phase 2, we are hoping to work even more closely with these sectors so that our work may have lasting impact in Singapore and beyond. If you are involved in these areas, we would be very interested to hear from you to explore opportunities for collaboration and information sharing.

I hope I have encouraged you to read more about CARES' latest work and achievements in this report. As ever, please do get in touch if you would like to know more about our work or have ideas for collaboration.

Professor Markus Kraft, CARES Director
March 2019



ABOUT US

Cambridge CARES is the University of Cambridge's presence in Singapore

The Cambridge Centre for Advanced Research and Education in Singapore (CARES) is a wholly-owned subsidiary of the University of Cambridge. Cambridge CARES is funded by the National Research Foundation as part of CREATE (Campus for Research Excellence and Technological Enterprise). We have a number of research collaborations between the University of Cambridge, Nanyang Technological University, the National University of Singapore and industrial partners.

The first programme administered by CARES is the Cambridge Centre for Carbon Reduction in Chemical Technology (C4T). The C4T programme is a world-leading partnership between Cambridge and Singapore, set up to tackle the environmentally relevant and complex problem of assessing and reducing the carbon footprint of the integrated petro-chemical plants on Singapore's Jurong Island. It brings together researchers from chemical engineering, biotechnology, chemistry, biochemistry, information engineering, electrical engineering, materials science and metallurgy.

The motivation for the C4T project is to integrate materials design and selection (i.e. for adsorbents

and catalysts) with advances in process design to achieve improved selectivity and conversion. Such improvements will provide a reduced carbon footprint and energy demand for both established and new processes. Lowering the cost of CO₂ capture, and technologies and strategies for waste heat utilisation are also underlying drivers in the research. Our six collaborative Interdisciplinary Research Programmes (IRPs) combine state-of-the-art experimental analysis with advanced modelling research from Cambridge and Singapore. Whilst each IRP has clearly defined milestones and deliverables, denoted as work packages (WPs), there is significant interaction between the IRPs.

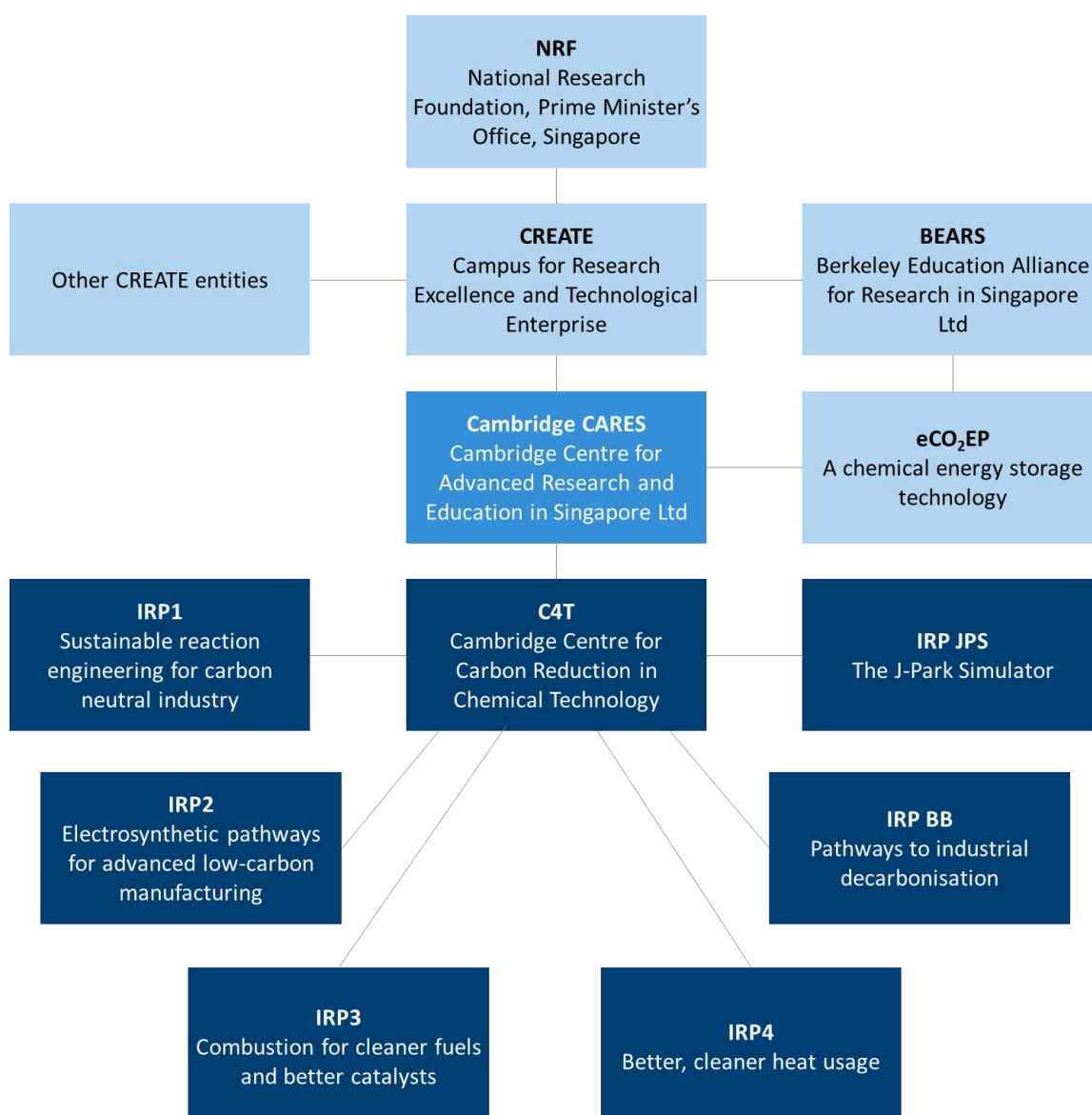
The first five-year research phase of C4T came to an end in October 2018. The programme received a further five years of funding for Phase 2, which commenced in November 2018.

This report is a summary of our last half-year of research progress. It includes scientific updates from each of our researchers, along with abstracts and figures from our recent publications. There are also several articles that explain the fundamental science behind some of our work, and the impact this can have on carbon reduction.



C4T answers the question of how to positively contribute to Singapore's ratification of the Paris Agreement on climate change while ensuring the country's progress and prowess in economic, technological, environmental and social dimensions. C4T Phase 2 systematically investigates the raw materials, processes and products of the local chemical industry and investigates technologies to lower the carbon footprint of this major pillar of Singapore's economy.

The second programme administered by CARES is eCO₂EP. This is a three-year programme that brings together researchers from the University of Cambridge, the University of California, Berkeley, the National University of Singapore and Nanyang Technological University to develop ways of transforming carbon dioxide emitted as part of the industrial process into compounds that are useful in the chemical industry supply chain.





Coupling orientation and mediation strategies for efficient electron transfer in hybrid biofuel cells

Kamal Etozarakji^{1,2*}, Daojian Cheng^{2,3}, Adrian C. Fisher^{2,3*} and Jong-Min Lee^{1,2*}
Enzymes are promising electrocatalysts for electron transfer (ET) in many biological processes. Strategies to enhance ET between enzymes and electroactive surfaces include orientation and immobilization of the enzymes and electron mediation achieved by the synthesis of a redox mediator on electrodes based on carbon nanotubes. This mediator (2,2'-methylenebis[3-(4-ethylthiazolium-5-yl)acrylate] (METS)) and an electropolymerizable monomer (pyrrole). The coupling of an enzymatic orientation and a mediated ET in the same chemical structure (pyrrole-ABTS-pyrrole (pyr-ABTS-pyr)) provides a much-improved performance. In a proton-exchange membrane hydrogen/oxygen fuel cell, the synthesized biohybrid provides a power density of 1.07 mW cm⁻² and 2.9 mW cm⁻², respectively. The principle of coupling an enzyme orientation and a redox mediator allows a great variety of mediators to be engineered and provides vast possibilities for the development of new devices.

* Among these methods, DEF is influenced strongly

Flexoelectricity and the Formation of Carbon Nanoparticles in Flames

Jacob W. Martin^{1,2*}, Maria Botero², Radomir L. Slavchev^{1,3}, Kimberly Bowal², Jethro Akroyd¹, Sebastian Mosbach¹, and Markus Kraft^{1,2,3,4*}

¹Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, CB3 0AS, U.K.; ²Cambridge Centre for Advanced Research and Education in Singapore (CARES), Singapore 117576; ³Department of Mechanical Engineering, National University of Singapore, Singapore 117576; ⁴School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459

ABSTRACT: The formation of carbon nanoparticles in flames involves a complex interplay of physical and chemical processes. It is known to depend on the fuel composition, the flow conditions, and the presence of aromatic compounds. We present a study of the formation of carbon nanoparticles in flames using a combination of experimental and computational approaches. We imaged the nascent carbon nanoparticles using a transmission electron microscope. The majority of nascent carbon nanoparticles are spherical and strongly oriented with respect to the flow direction. The results indicate that the interaction between flexoelectricity and the interaction between fullerenes-like polar aromatics and chemi-ions is critically assisting the nucleation and growth of carbon nanoparticles.

HIGHLIGHTS

ARTICLE [DOI: 10.1038/s41467-018-06769-9](https://doi.org/10.1038/s41467-018-06769-9) OPEN

Hydrogen spillover through Matryoshka-type (ZIFs@ZIFs)

OUTSTANDING WORK FROM THE LAST SIX MONTHS OF CAMBRIDGE CARES RESEARCH

REVIEW **H₂O₂ Production**

Selective Electrochemical H₂O₂ Production via Two-Electron Oxygen Electrochemistry

Yuanyuan Jiang, Pengjuan Ni, Chuanxia Chen, Yizhong Biao Kong, Adrian Fisher, and Xin Wang*

Direct electrochemical production of hydrogen peroxide (H₂O₂) through two-electron oxygen electrochemistry, for example, the oxygen reduction in fuel cells or water oxidation in water electrolyzers, could provide an attractive alternative to locally produce this chemical on demand. The efficiency of these processes depends greatly on the availability of cost-effective catalysts with high selectivity, activity, and stability. In recent years, various novel nanostructured materials have been reported to selectively produce H₂O₂. Through combined experimental and theoretical approaches, underlying mechanisms in the electrochemical and theoretical approaches, electrochemistry have been unveiled. Considering the remarkable progress in this area, the authors summarize recent developments regarding the production of H₂O₂ through two-electron electrochemical oxygen reactions. The fundamental aspects of electrochemical oxygen reactions are introduced. Various types of electrochemical oxygen reactions are first two-electron oxygen electrochemistry that can effectively produce H₂O₂ via unique structure-, component-, and composition-dependent electrochemical performance together with the underlying catalytic mechanisms are discussed. Finally, a brief conclusion about the recent progress achieved in electrochemical generation of H₂O₂ and an outlook on future research challenges are given.

Dr. Y. Y. Jiang, Dr. P. J. Ni, Dr. C. X. Chen, Prof. Y. Z. Lu, Prof. P. Yang
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the instability of H₂O₂ in acidic media. Therefore, there is increasing interest in low-cost and decentralized production of H₂O₂ to greatly reduce the cost of H₂O₂.

Automated chemical routes for a sustainable chemical industry

Dr Zhen GUO, Senior Research Fellow, IRP1

The chemical industry relies heavily on the processing of fossil fuels and has a high carbon footprint as a result. Rapid change is required to reduce this carbon footprint and its impact on the planet.

One way to do this is through using industrial waste products, e.g. carbon dioxide, as feedstocks for the production of value-added chemicals, instead of dumping them into the environment. A new approach is now allowing for faster exploration of the various options for valorisation of industrial wastes—the automated chemical route (ACR) technique.

Developed by Prof. Alexei LAPKIN (PI, University of Cambridge) and his research group, the ACR technique is able to link majority kinds of feedstocks to target products. Therefore, studying feedstocks such as CO₂, CH₄ and compounds from bio-wastes may uncover new sustainable chemical routes that could potentially replace current industrial routes and improve carbon footprint records. Compared to a conventional human-based research strategy, the likelihood for identification of new chemical routes can be significantly enhanced by the ACR technique.

Because of their high complexity, reaction networks containing millions of reactions are not possible for humans to examine. ACR can provide a bird's-eye view of the whole picture with the aid of computers. Several interesting chemical routes that begin with CO₂ have already been identified through exhaustive mining of a large chemical database. Further discovery of these routes could challenge manual searching in speed and efficiency.

Relevant publications

Jacob, Philipp-Maximilian, et al. 2018. "Statistics of the network of organic chemistry." *Reaction Chemistry & Engineering*. <https://doi.org/10.1039/C7RE00129K>.

Lapkin, Alexei A., et al. 2017. "Automation of route identification and optimisation based on data-mining and chemical intuition." *Faraday Discussions*. <https://doi.org/10.1039/C7FD00073A>.

Dr Zhen Guo obtained his Bachelor and Master degrees in chemistry at Wuhan University, China, and his PhD degree in chemical engineering at Nanyang Technological University, Singapore. He has been working in industry and academia for eight years. Dr Guo was a trained chemical engineer in heterogeneous catalysis and now is interested in computer aided chemical processes design.



Purifying the air with catalytic oxidation

Shuyang WU, PhD student, IRP3

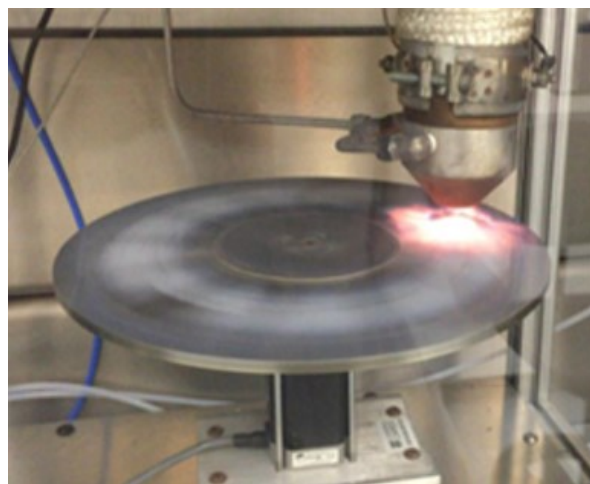
Volatile organic compounds (VOCs) are prevalent components of indoor air pollution. They are commonly found in the indoor air of residences and office buildings, as well as in various industrial processes, waste streams and disposal facilities. Many VOCs can cause headaches, dizziness and eye, nose and throat irritation.

Traditional methods for removing VOCs include absorption, incineration and condensation but these have inherent limitations, such as high costs, short and unpredictable life spans and secondary pollution. In recent years, photocatalytic oxidation (PCO) and photochemical oxidation have been extensively studied as promising methods for removing and destroying various VOCs in polluted air and converting them into benign and odourless constituents, like water vapour.

Relevant publication

Wu, Shuyang, et al. 2018. "Premixed stagnation flame synthesized TiO₂ nanoparticles with mixed phases for efficient photocatalytic hydrogen generation." *ACS Sustainable Chemistry & Engineering*. <https://doi.org/10.1021/acssuschemeng.8b03142>.

Semiconductor-based photodegradation has been attracting a great deal of interest. Among the plentiful semiconductor materials, titanium dioxide (TiO₂) has been regarded as one of the most promising photocatalysts for the degradation of pollutants in water and air, because of its physical and chemical stability, easy availability, nontoxicity and unique electronic and optical properties. PCO using TiO₂ is cost-effective and can be carried out at room temperature and atmospheric pressure, and is a promising way to purify the air and protect the environment.



Flame synthesising TiO₂.



Shuyang Wu is a PhD student at Nanyang Technological University. His main research interest lies in the area of flame synthesised metal oxide for the application in energy and environment. He is currently using the continuous one-step flame synthesis method to prepare mixed-phase TiO₂ nanoparticles with excellent performance in renewable energy production.

FOCUS ON

FUNDAMENTAL SCIENCE

A computational microscope peers into charcoal's nanostructure

PhD student Jacob MARTIN (IRP3) explains recent insights into the nanostructure of charcoal and its implications for carbon capture

A puzzle has perplexed carbon scientists for the last 70 years: why do some carbon materials not turn into graphite when heated, as most others do? We have recently peered into charcoal's nanostructure using a "computational microscope", providing insights into this puzzle with implications for slowing climate change.

Rosalind Franklin first posed this puzzle in 1951. In 1941, she began her PhD research and, wanting to contribute to the war efforts, started her studies at the British Coal Utilisation Research Association on the porosity of coals. She found that upon heating, coal's pores became smaller. This allowed her to characterise coals for



Jacob MARTIN is a PhD student at the University of Cambridge. He completed a BSc with chemistry and physics followed by a MSc in chemistry at the University of Auckland.

gas mask applications, greatly impacting the war effort, while also writing five landmark papers and completing her PhD in 1945. A year later she was awarded a position in Jacques Mering's laboratory in Paris. There, she learnt the art of collecting photographs of X-rays scattered off materials – crystallography.

Earlier, the study of X-ray patterns collected from carbon materials had yielded the arrangement of atoms in diamond (Bragg, 1913) and graphite (Bernal, 1924). Analysis of soot, charcoals or coals showed only minimal graphitic ordering with Warren determining in 1934 that small, misaligned crystallites of graph-

Rosalind Franklin in Mering's laboratory, Paris.



ite were the building blocks of these disordered carbons. Franklin was able to collect some excellent X-ray patterns of carbon materials throughout their carbonisation that converted into graphite upon heating. In her landmark 1951 paper she details a surprising finding: some materials, when heated, will not convert into graphite. She called these non-graphitising. As graphite is the most stable phase of carbon at atmospheric pressure, it was puzzling that a metastable form of carbon would be the end product of such high-temperature treatment, which should yield the most thermodynamically stable structure. How are the atoms arranged in these carbons that inhibits graphitisation?

In the years since Franklin’s paper, many uses for these non-graphitising carbons have been developed: activated carbon for water and gas purification, electrodes for batteries, high temperature ceramics for smelting, electrodes for electrochemical and biological sensing and biologically compatible, robust materials for prosthetics. Yet a comprehensive molecular model that could capture this vastly tunable class of materials was lacking.

CARES researchers teamed up with the Carbon group at Curtin University’s physics department to develop a computational microscope able to peer into this elusive structure. The Curtin group had mathematically described the carbon-carbon bond breaking and forming and ran large-scale simulations with thousands of carbon atoms that allowed virtual carbon models to be generated in the computer. The models were produced at a range of densities, from activated carbons (0.5 g/cc) to charcoal and glassy carbon densities (1.5 g/cc) that closely matched all experimental measures. Importantly, we did not predefine the arrangement of the atoms but allowed random thermal movements to self-assemble these 3D nanostructures. When viewing these structures it is important to mention that they were performed with periodic boundaries, so while it might appear that the sheets disappear out of the simulation box, they are in fact connected to the sheets on the opposite side of the simulation box (image below).

Armed with these accurate models we worked together to analyse these beautifully complex arrangements of atoms using the mathematics of

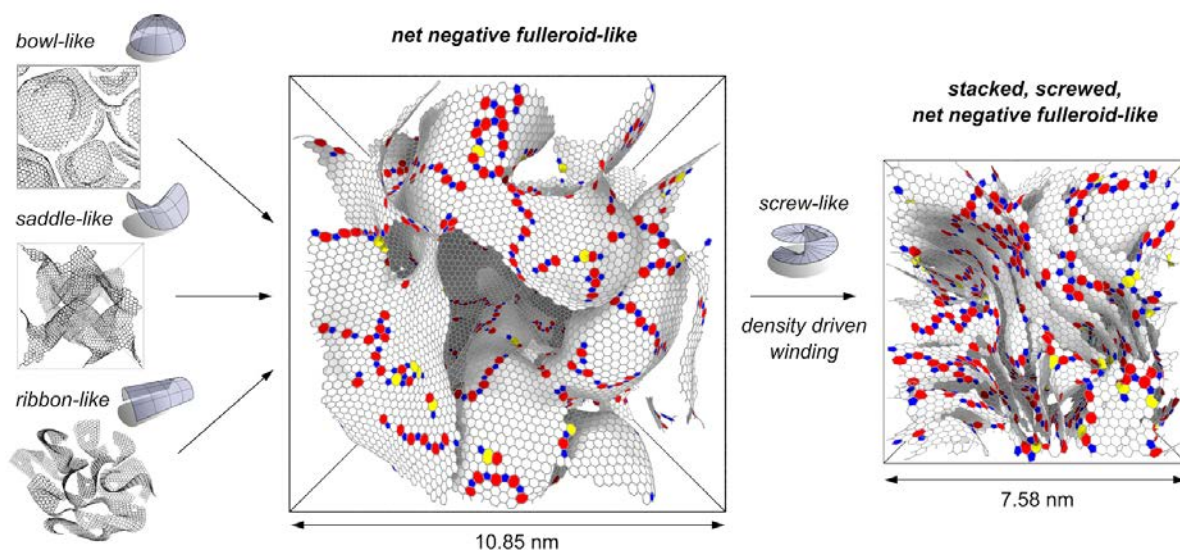
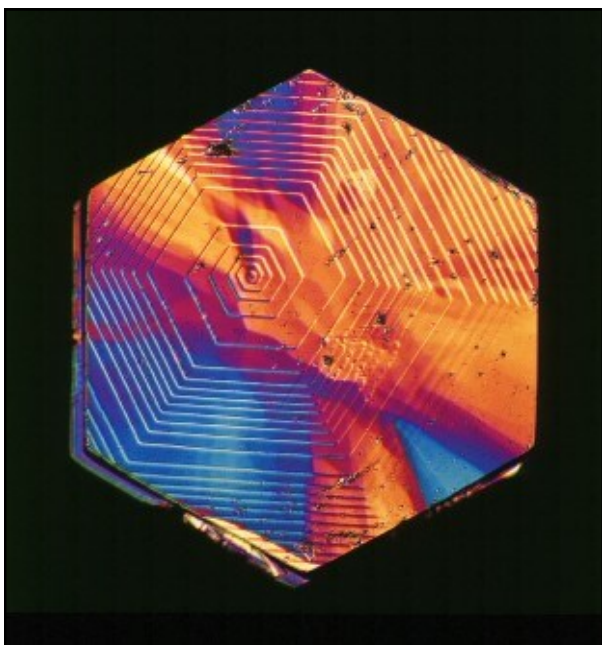


Diagram showing the three shapes found in the self assembled nanocarbon models. Screw defects are found to give rise to the layered regions.

geometric topology. Firstly, we found that graphene sheets with hexagonal arrangement of carbon atoms dominated. However, considerable warping and bending of the sheets was allowed for by a small number of non-hexagonal rings (coloured in the previous image) that integrate either bowl shaped or saddle shaped curvatures. We found an excess of the saddle shapes, which is critical for allowing the sheets to connect in three dimensions. This net negative curvature is suggested to be the distinguishing feature of this type of carbon.

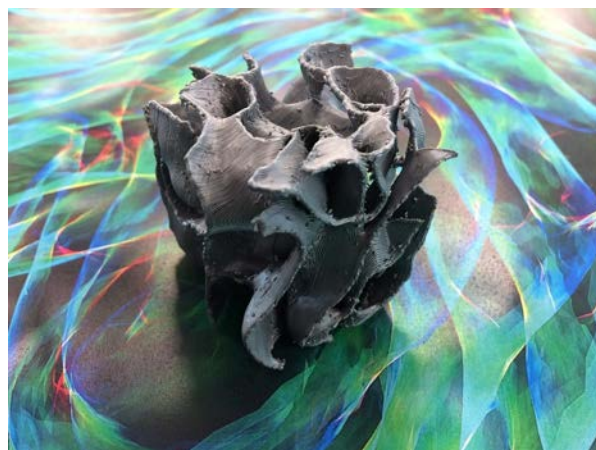
At low densities the structures are highly porous, with the sheets held apart by the connectivity of the network. When increasing the density past 0.9 g/cc we found that screw defects become integrated that allow for a winding up of the structure into layered ribbon regions. These screw defects are well known to be present in graphite (see image below). These stacked regions fill all of the available pores and make the structure non-porous. They also provide the misaligned regions of graphitic ordering that Franklin described as crystallites.



Screw defect in graphite captured using polarised light microscopy.

Image credit: © John A. Jaszczak. Used with permission.

In terms of graphitizability, the connectivity of the network would require all bonds to be broken along one axis to allow conversion into graphite. This requires a considerable energetic barrier to graphitisation and provides a possible explanation for their non-graphitizability. However, more work is needed to be done on how curvature is integrated into these structures to allow for the prediction of graphitizability of any precursor and the tuning of their nanoscale properties.



3D printed model of 0.5 g/cc model for non-graphitising carbon.

These nanoscale understandings have a macroscale impact on the climate. Charcoal is actually a stable store of atmospheric carbon. Biomass photosynthetically traps carbon and heating without air converts some the carbon into a very stable material that will not break down and release the carbon back into the atmosphere. The models help us to understand the oxidation resistance of these materials as the curvature reduces the number of reactive edges, allowing for the thousands of year of stability. We also hope that by understanding the nanostructure we can upgrade charcoal into higher value products such as battery anodes or activated carbons for water and air purifications. Biochar is also beneficial to soils and understanding how to tune the nanostructure for optimal soil improvements relies on these detailed descriptions. Finally, being able to monetise biochar will increase the rate of adoption and speed up the carbon capture potential of this technology.

Highlighted research outputs from November 2018 - March 2019

A selection of our top publications and research highlights from across the programme.

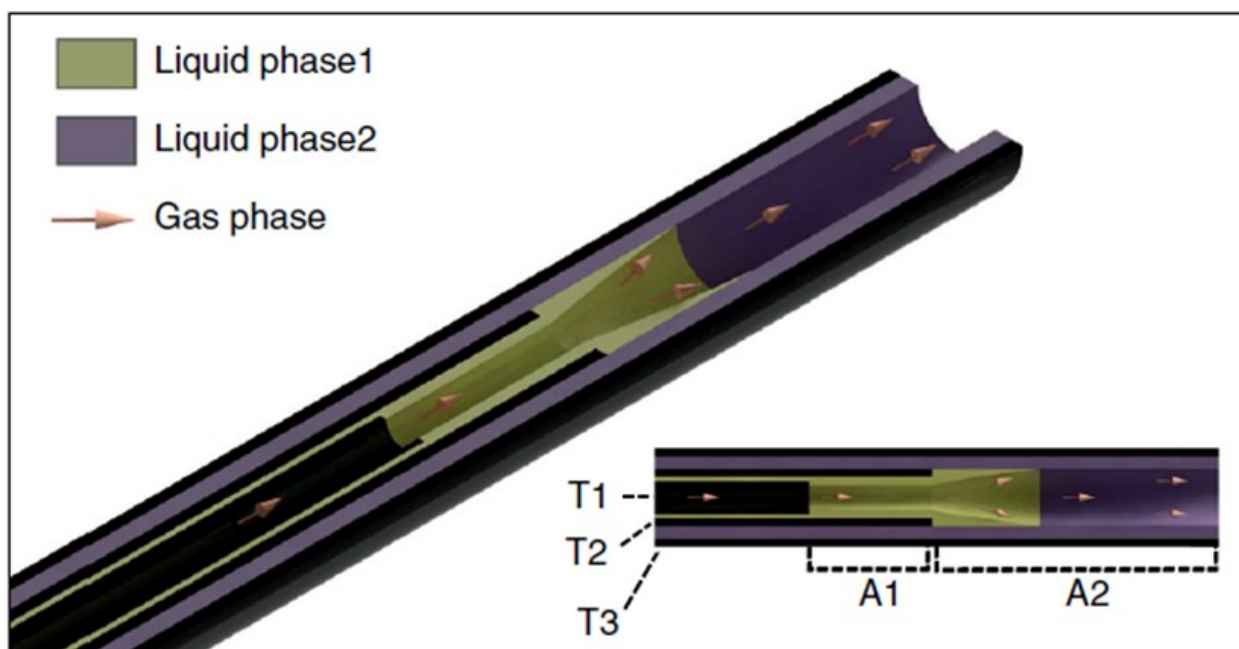
IRP1: Hydrodynamic assembly of two-dimensional nanostructures

Nicholas Jose, Hua Chun Zeng and Alexei Lapkin, *Nature Communications*

DOI: 10.1038/s41467-018-07395-4

Formation mechanisms of two-dimensional nanostructures in wet syntheses are poorly understood. Even more enigmatic is the influence of hydrodynamic forces. Here we use liquid flow cell transmission electron microscopy to show that layered double hydroxide, as a model material, may form via the oriented attachment of hexagonal nanoparticles; under hydrodynamic shear, oriented attachment is accelerated. To hydrodynamically manipulate the kinetics of particle

growth and oriented attachment, we develop a microreactor with high and tunable shear rates, enabling control over particle size, crystallinity and aspect ratio. This work offers new insights in the formation of two-dimensional materials, provides a scalable yet precise synthesis method, and proposes new avenues for the rational engineering and scalable production of highly anisotropic nanostructures.



Annular reactor mixing dynamics: Schematic of microreactor axial cross-section, where T1, T2, and T3 are the three coaxial tubes, and regions A1 and A2 are the annular flow regions created by the flow of the gas phase (red arrow). In A2, mixing of phase 1 (yellow) and phase 2 (purple) occur.

IRP1: Architecture and preparation of hollow catalytic devices

Bowen Li and Hua Chun Zeng, *Advanced Materials*

DOI: 10.1002/adma.201801104

Since pioneering work done in the late 1990s, synthesis of functional hollow materials has experienced a rapid growth over the past two decades while their applications have been proven to be advantageous across many technological fields. In the field of heterogeneous catalysis, the development of micro- and nanoscale hollow

materials as catalytic devices has also yielded promising results, because of their higher activity, stability, and selectivity. Herein, the architecture and preparation of these catalysts with tailorable composition and morphology are reviewed. First, synthesis of hollow materials is introduced according to the classification of tem-

plate mediated, template free, and combined approaches. Second, different architectural designs of hollow catalytic devices, such as those without functionalization, with active components supported onto hollow materials, with active components incorporated within porous shells, and with active components confined within interior cavities, are evaluated respectively. The observed catalytic performances of this new class of catalysts are correlated to structural merits of individual configuration. Examples that demonstrate synthetic approaches and architected configurations are provided. Lastly, possible future directions are proposed to advance this type of hollow catalytic devices on the basis of our personal perspectives.

Schematic illustration of hollow catalytic devices with different structural configurations.



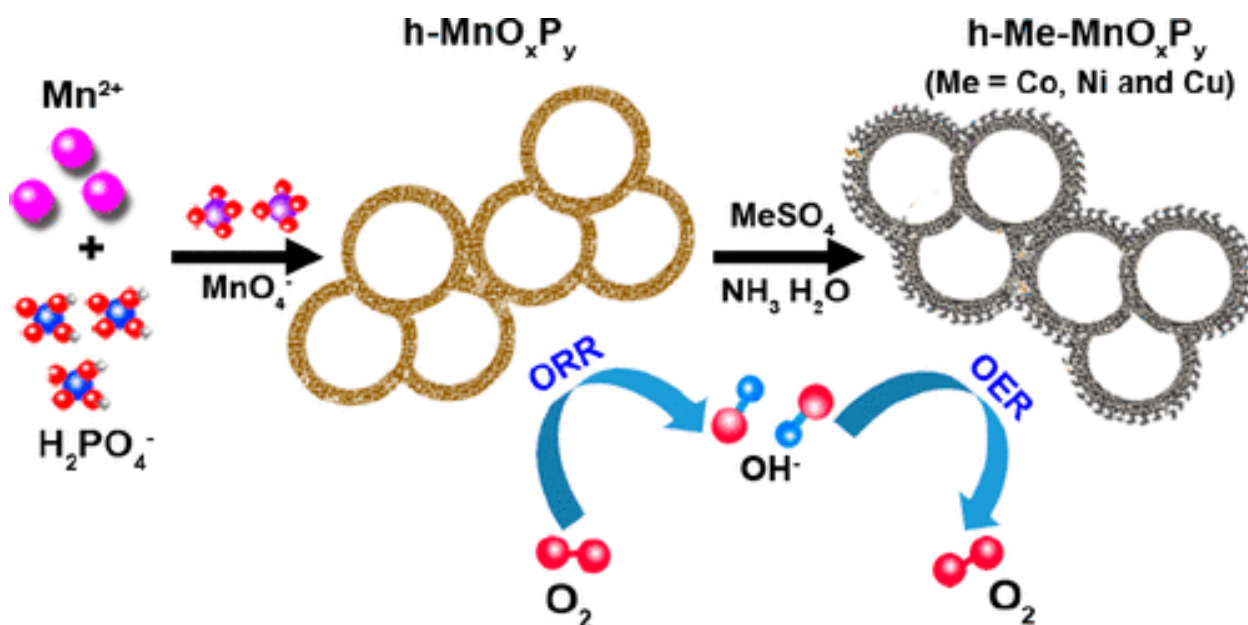
IRP2: A self-templating redox-mediated synthesis of hollow phosphated manganese oxide nanospheres as noble-metal-like oxygen electrocatalysts

Tianran Zhang, Shengliang Zhang, Sheng Cao, Qiaofeng Yao and Jim Yang Lee, *Chemistry of Materials*

DOI: 10.1021/acs.chemmater.8b03681

The development of low-cost, high-performance electrocatalysts for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) to replace the use of noble metals is a challenge for the rechargeable metal-air batteries. Although manganese compounds, oxides in particular, have drawn the most interest, they rarely deliver

the same performance as the noble metals in oxygen electrocatalysis, notwithstanding the enhancements introduced by nanosizing and adjuvant metal doping. Herein, we report a noble-metal-like performance for manganese oxide catalysts by combining phosphate modification with a hollow nanostructure. A simple and scalable



self-templating method based on phosphate-mediated Mn redox reactions was developed for the preparation of hollow phosphated manganese oxide nanospheres at room temperature. A series of simple (h-MnO_xP_y) and complex phosphated manganese oxide (h-Me-MnO_xP_y, Me = Co, Ni, Cu) hollow nanospheres can be produced more efficiently than normal hollow nanostructure construction techniques based on hard and soft templates and hydrothermal Ostwald ripening. Among the hollow phosphated manganese ox-

ides h-MnO_xP_{0.21} delivered the best ORR performance (half-wave potential of 0.85 V vs RHE, similar to 20 wt % Pt/C) and h-Co-MnO_xP_{0.21} the best OER performance (1.60 V vs RHE for 10 mA cm⁻², marginally higher than 20 wt % Ir/C). Small charge-discharge voltage gaps (ΔV) were shown in both alkaline ($\Delta V = 0.72$ V at 5 mA cm⁻²) and neutral ($\Delta V = 1.28$ V at 1 mA cm⁻²) rechargeable Zn-air batteries with the combined use of these catalysts, similar to the 20 wt % Pt/C + 20 wt % Ir/C combined catalytic systems.

IRP2: Selective electro-reduction of carbon dioxide to formic acid on cobalt-decorated copper thin films

Research highlight suggested by Dr DAI Chencheng

- The CuCo electrode was prepared through the electrodeposition of cobalt on the surface of copper, followed by Ar and air atmosphere treatment.
- The as-prepared catalyst exhibits selective conversion of CO₂ to formic acid with a Faradaic efficiency of ca. 80% at applied potential of -0.65 V vs. reversible hydrogen electrode.
- DFT calculation proves that the decoration of Co on Cu promotes the formation of COOH*/HCOO* and impede H₂ formation when catalysed, and the higher formic acid selectivity is achieved as a result.
- This work represents a strategy for designing a CO₂ reduction electrocatalyst.

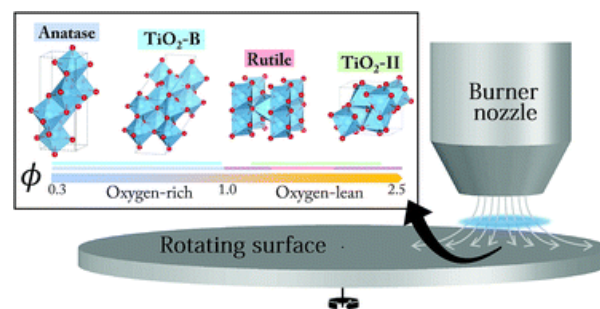
IRP3: Polymorphism of nanocrystalline TiO₂ prepared in a stagnation flame: formation of the TiO₂-II phase

Manoel Manuputty, Jochen Dreyer, Yuan Sheng, Eric Bringley, Maria Botero, Jethro Akroyd and Markus Kraft, *Chemical Science*

DOI: 10.1039/C8SC02969E

A metastable "high-pressure" phase known as α -PbO₂-type TiO₂ or TiO₂-II is prepared via a single-step synthesis using a laminar premixed stagnation flame. Three other TiO₂ polymorphs, namely anatase, rutile and TiO₂-B phases, can also be obtained by tuning the oxygen/fuel ratio. TiO₂-II is observed as a mixture with rutile under oxygen-lean flame conditions. To the best of our knowledge, this is the first time that this phase has been identified in flame-synthesised TiO₂. The formation of TiO₂-II in an atmospheric pressure flame cannot be explained thermodynamically and is hypothesised to be kinetically driven through the oxidation and solid-state transformation of a sub-oxide TiO_{2-x} intermediate. In this scenario, rutile is nucleated from the metastable

TiO₂-II phase instead of directly from a molten/amorphous state. Mixtures containing three-phase heterojunctions of anatase, rutile, and TiO₂-II nanoparticles as prepared here in slightly oxygen-lean flames might be important in photocatalysis due to enhanced electron-hole separation.

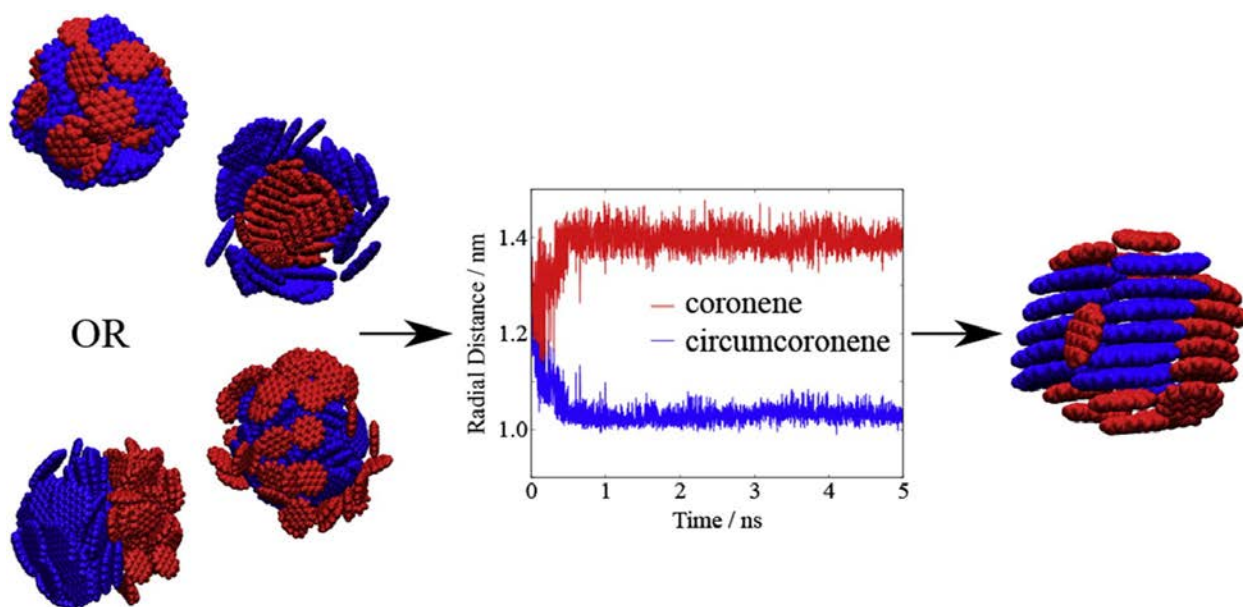


IRP3: Partitioning of polycyclic aromatic hydrocarbons in heterogeneous clustersKimberly Bowal, Jacob W. Martin and Markus Kraft, *Carbon*

DOI: 10.1016/j.carbon.2018.11.004

The morphologies of heterogeneous clusters of polycyclic aromatic hydrocarbons (PAHs) are investigated using molecular modelling. Clusters of up to 100 molecules containing combinations of the different sized PAHs circumcoronene, coronene, ovalene, or pyrene are evaluated. Replica exchange molecular dynamics simulations using an all-atom force field parameterised for PAHs sample many configurations at high and low temperatures to determine stable low energy structures. The resulting cluster structures are

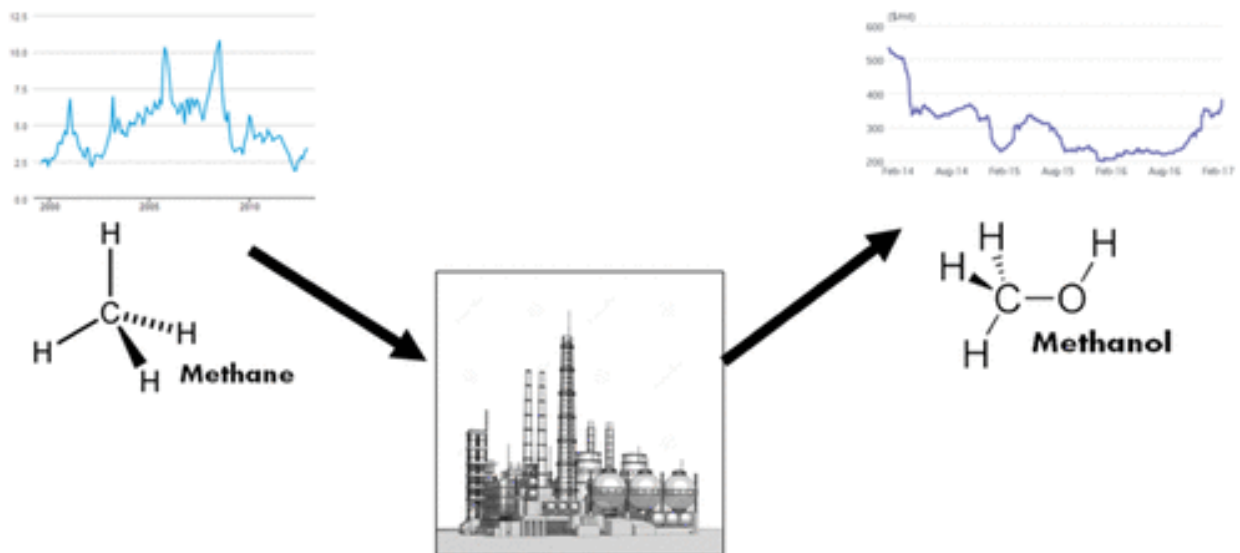
evaluated using molecular radial distances and coordination numbers, and are found to be independent of initial configuration and the cluster sizes studied. Stable clusters consist of stacked PAHs in a core-shell structure, where the larger PAHs are found closer to the cluster core and the smaller PAHs are located on the cluster surface. This work provides novel insight into the molecular partitioning of heterogeneous aromatic clusters, with particular relevance to the structure of nascent soot particles.

**IRP JPS: Enhanced procurement and production strategies for chemical plants: utilizing real-time financial data and advanced algorithms**Janusz Sikorski, Oliver Inderwildi, Mei Qi Lim, Sushant S. Garud, Johannes Neukäufer and Markus Kraft, *Industrial & Engineering Chemistry Research*

DOI: 10.1021/acs.iecr.8b02925

This paper presents an implementation of an automated algorithm powered by market and physical data to improve procurement and production of a chemical plant with the goal of improving the overall economics on the entity. Herein, the algorithm is applied to two scenarios that serve as case studies: conversion of natural gas to methanol and crude palm oil to biodiesel. The

program anticipates opportunities to increase profit or avoid loss by analysing the futures market prices for both reagents and the products while considering cost of storage and conversion derived from physical simulations of the chemical process. Analysis conducted on June 11, 2018, in the biodiesel scenario shows that up to 219.28 USD per tonne of biodiesel can be earned by buy-



ing contracts for delivery of crude palm oil in July 2018 and selling contracts for delivery of bio-diesel in August 2018 which equates to a margin 11.6% higher than in case of the direct trade. Moreover, it is shown that losses of up to 11.3% can be avoided, and therefore, it is shown that there is realistic scope for increasing the profitability of a chemical plant by exploiting the opportunities across different commodity markets in an automated manner. Consequently, such a cyber

system can be used to assist eco-industrial parks with supply chain management, production planning, as well as financial risk governance and, in the end, help to establish a long-term strategy. This study is part of a holistic endeavor that applies cyber-physical systems to optimise eco-industrial parks so that energy use and emissions are minimised while economic output is maximised.



Members of the JPS team use the J-Park Simulator.

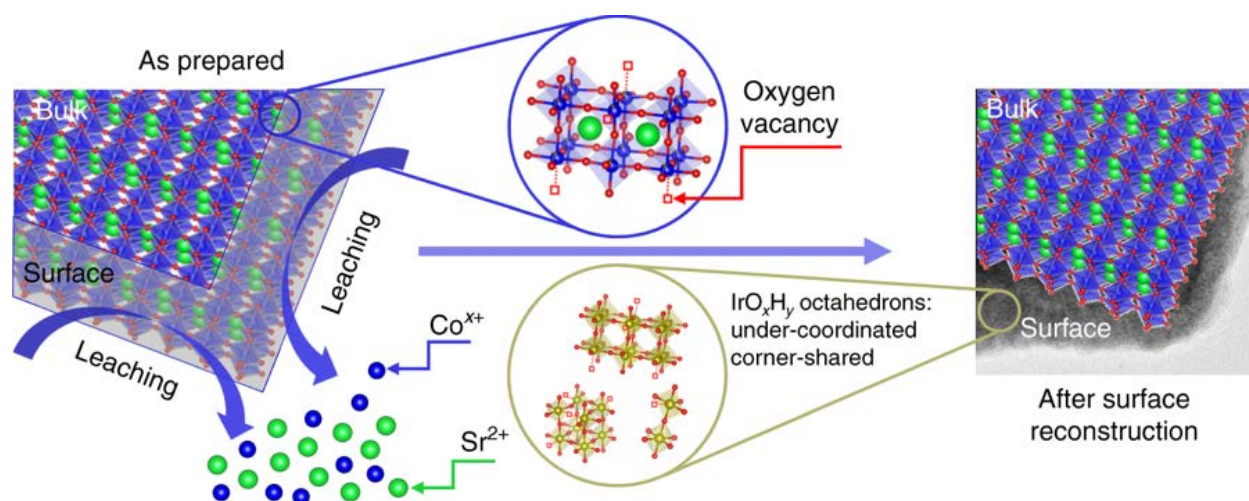
eCO₂EP: Exceptionally active iridium evolved from a pseudo-cubic perovskite for oxygen evolution in acid

Yubo Chen, Haiyan Li, Jingxian Wang, Yonghua Du, Shibo Xi, Yuanmiao Sun, Matthew Sherburne, Joel W. Ager, Adrian C. Fisher and Zhichuan J. Xu, *Nature Communications*

DOI: 10.1038/s41467-019-08532-3

Exploring robust catalysts for water oxidation in acidic electrolyte is challenging due to the limited material choice. Iridium (Ir) is the only active element with a high resistance to the acid corrosion during water electrolysis. However, Ir is rare, and its large-scale application could only be possible if the intrinsic activity of Ir could be greatly enhanced. Here, a pseudo-cubic SrCo_{0.9}Ir_{0.1}O_{3-δ} perovskite, containing corner-shared IrO₆ octahedrons, is designed. The Ir in the SrCo_{0.9}Ir_{0.1}O_{3-δ}

catalyst shows an extremely high intrinsic activity as reflected from its high turnover frequency, which is more than two orders of magnitude higher than that of IrO₂. During the electrochemical cycling, a surface reconstruction, with Sr and Co leaching, over SrCo_{0.9}Ir_{0.1}O_{3-δ} occurs. Such reconstructed surface region, likely contains a high amount of structural domains with corner-shared and under-coordinated IrO_x octahedrons, is responsible for the observed high activity.





IRP1

SUSTAINABLE REACTION ENGINEERING FOR CARBON NEUTRAL INDUSTRY

IRP1 is focused on chemical technologies that allow rapid de-carbonisation of chemical industry and the chemical supply chain. Our target is to deliver innovative solutions to direct utilisation of carbon dioxide as a feedstock, as well as to significantly increase the efficiency in conversion of methane to bulk intermediates. We are also exploring the options for the emerging circular economy, by developing new transformations of molecules available in different bio-waste resources into high-value functional molecules. Potential impact on carbon emissions reduction is evaluated by life cycle assessment tools.

IRP1 Principal Investigators:



*Professor Alexei LAPKIN
University of Cambridge*



*Asst Professor Paul LIU Wen
Nanyang Technological University*



*Professor ZENG Hua Chun
National University of Singapore*



OVERVIEW

The start of Phase 2 of the C4T project for IRP1 combines continuation of several PhD projects in NUS, NTU and Cambridge, continuous work of two post-docs (Dr Yong YAN and Dr Polina YASENEVA), and the start of a new \$250k SMART Innovation Centre collaborative project 'Rapid industrialisation of next generation nano materials' that emerged from Phase 1 and is being led by Nicholas JOSE (Research Assistant, CARES).

In the SMART project, IRP1 has extended collaboration to A*STAR SIMTech. The project will develop a method of manufacturing functional nanomaterials for applications in healthcare. It is an 18-month project which is employing an engineer and will host an intern over the summer of 2019.

In the Cambridge-based project, Dr Polina YASENEVA is focusing on the topic of evaluating sustainability of the new circular economy technologies. This project is a direct link to Work Package 2 work done in Singapore on developing new routes for valorisation of bio-waste. The methods of assessment developed by Dr Yaseneva will later be used in the work of WP2 researchers. The ongoing project is focusing on the waste of wood processing, which is highly relevant to the South East Asia region.

In the NUS-based projects the focus is on innovative nano-architectures for enhancing selectivity and productivity of the CO₂ conversion catalysts. This work will be later in the project linked with

scale-up of materials synthesis to develop industry-ready catalytic materials. The second workstream of the NUS-based projects is on bio-waste conversion. At present we are undertaking an overview of the regionally-available bio-waste streams and the molecular structures available in them.

In the NTU-based projects the focus is on developing new reaction concepts supported by materials with reversible chemical storage capability, so called chemical-looping technology.

In Phase 2 a number of projects are industry-funded. This allowed us to expand into new methodologies. New to IRP1 are the projects on 'big data' and 'machine learning', the methodologies that we intend to apply for developing new reaction pathways for valorisation of bio-waste in WP2 (led by Dr Zhen GUO, Research Fellow) and increasing the speed of developing nanomaterials (led by Liwei CAO, PhD student). Both projects are funded by BASF. The new Cambridge-CARES PhD student Perman JORAEV has also started a project on machine learning for faster process development and is currently working on valorisation of bio-waste. His project is funded by UCB.

Professor Alexei Lapkin, PI
University of Cambridge

Update on work package 1.1

Design of nano-structured catalysts

Runze QIN (PhD student, NUS) has been completing work on Covalent Organic Frameworks (COFs). COFs are composed of covalently bonded monomers, are a class of emerging porous crystalline materials drawing enormous attention in recent years for their tunable pore size and chemical functionalities. The structure of COFs can be tailored by selection of different building blocks due to high availability of suitable organic molecules, suggesting potential applications in gas adsorption, electronic devices and catalysts. Along with others in his research group, Runze encapsulated pre-synthesised nanoparticles with COF materials, thus imparting catalytic activity to COF materials. The thickness of COF shell can be controlled at a level of 20 nms, making each COF encapsulated nanoparticle a highly active nanoreactor. Using more sophisticated processes, the size and morphology of COF shell can be controlled. The COF shell can also serve as screening sieve to filter molecules with larger molecule size, making it a potential reactor with size selectivity. The functionality can be further enriched by additionally linking noble metal ions to nitrogen atoms in COF structure, allowing it to be a sustainable catalyst for a variety of reactions.

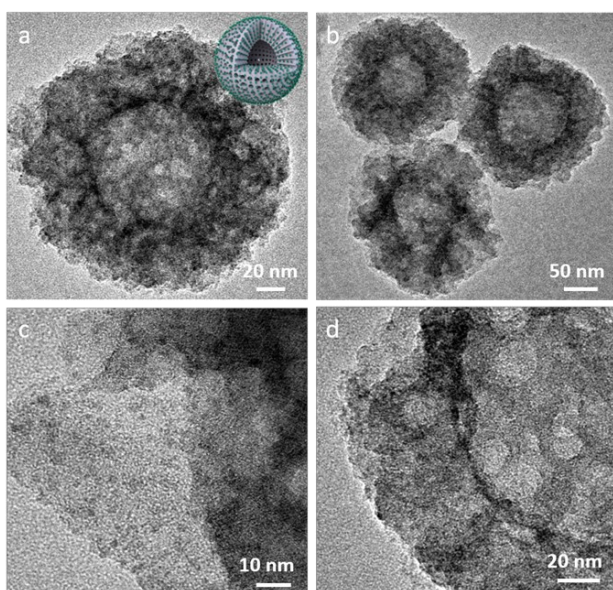


Fig. 1.2: TEM images of NPC/CoNiO_x heterostructure.

Jingjing WANG

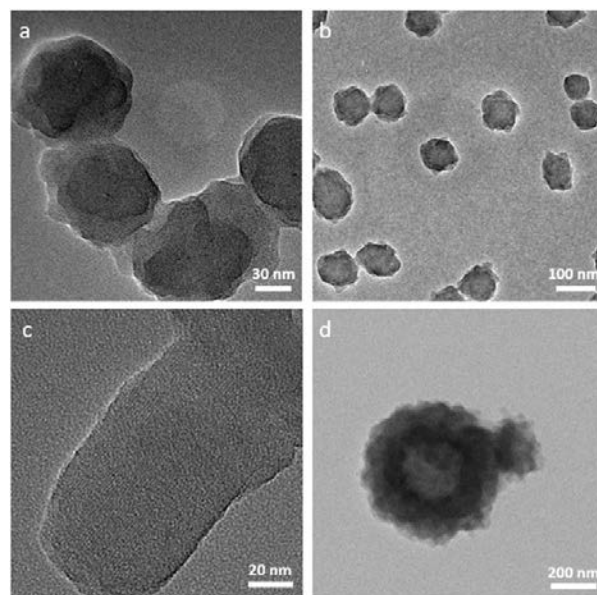


Fig. 1.1: **a, b** TEM image of COF encapsulated Pt nanoparticles, **c** rod like COF encapsulated Pt nanoparticles with lattice fringe, and **d** hollow COF sphere.

Runze QIN

Jingjing WANG (PhD student, NUS) is exploring the oxygen evolution reaction (OER), which is a critical element in many renewable energy technologies such as fuel cells, metal-air batteries and water electrolysis. However, its inherent sluggish kinetics of four-electron transfer process requires high overpotentials and thus results in considerable energy loss. To tackle this problem, great effort has been devoted to investigating active catalysts for OER over the past decades. To date, the most efficient catalysts for OER have been identified as noble metal oxides, such as IrO₂ and RuO₂. Nevertheless, these state-of-the-art catalysts are precious metal based and the metal scarcity has hampered their large-scale applications. Therefore, the development of cost-effective and high-performance OER electrocatalysts is of great importance.

A number of recent studies have shown that hybrid electrocatalysts, composed of earth-abundant transition metal (TM) oxides and heteroatom-doped (e.g., nitrogen-doped) carbonaceous materials, usually exhibit exceptional OER

activities and good stability superior to their single-component counterparts. The improved electro-chemical performance of the composites has been generally ascribed to the following: (1) The strong chemical bonding between metal-containing species and heteroatom doped-carbon supports can greatly facilitate the electron transfer, hence improving the conductivity for the hybrid electrocatalysts. (2) More importantly, the strong coupling between TM and heteroatom doped-carbon at the interface can normally induce a so-called synergistic effect for the hybrids, benefiting substantially enhanced oxygen electrochemistry compared to their dopant-free counterparts.

Jun Wen YEO (PhD student, NUS) successfully synthesised layered double hydroxides (LDHs) with flower-like structures to include a series of catalytically important transition metals (Cu, Co, Ni, Zn) as shown in Figure 1.3. Morphologically, LDHs generally adopt a 2D plate morphology, although a hierarchical 3D flower-like structure assembled from individual plates are also commonly reported in literature. For the purpose of catalysis, the flower-like morphology should be preferred due to its larger surface area. The 3D structure also retains the advantages of plate-like LDH (compositional flexibility, ultrathin layers) while circumventing its tendency to stack which diminishes active site exposure. However, whether the synthesised LDHs possess a plate or flower

In the last half year, Jingjing prepared a heterostructure coupling of N, P-doped mesoporous carbon spheres with fine transition metal oxides as highly active synergistic electrocatalysts. She found a strong synergistic effect for the hybrids, which results from the change of interface electron structure of transition metal oxides and N, P doped carbon. In addition, she further reported the facilitation role of dopant P to the synergistic effect, which have not been reported although N doped carbon is widely studied.

-like structure depends on the not just on the synthesis method but also the metal precursors used. For example, MgAl-LDH and CoAl-LDH with flower-like morphology can be synthesised with a one-pot solvothermal method where thermal decomposition of urea provides the precipitating basic conditions, while ZnAl-LDH tends to form highly dense microspheres consisting of severely agglomerated nanosheets instead of flower-like structures even when similar synthesis methods are employed. Further, NiFe-LDH requires the addition of a mineralising agent F^- in order to produce the flower-like structure. The synthesised LDH materials are tested for important CO_2 utilisation reactions such as CO_2 hydrogenation to methane and methanol.

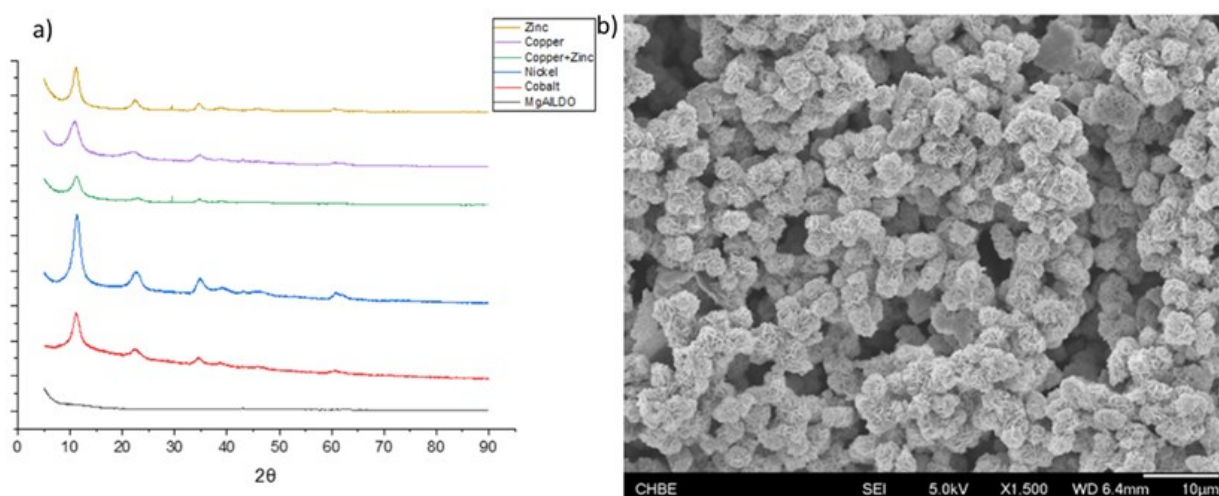


Fig. 1.3: **a** XRD and **b** FESEM images of transition metal doped LDH.

Jun Wen YEO

Update on work package 1.2

Novel reactions and functional molecules

Dr Polina YASENEVA (Research Fellow, CAM) is working on life cycle assessment models (LCA) for evaluation of environmental impacts of the new processes developed within IRP1. Current project is targeting the potential technology of utilising the large-scale bio-waste resource from paper manufacturing to produce high-value chemical intermediates, specifically to convert paper making waste into a chemical intermediate, nopinone. In the last six months process and LCA models were improved, and more data on filtration within the hot water process were collected and implemented in the model flowsheet and LCA. It was shown that the sequence of processing operations has a significant influence on the overall values of environmental impacts. For example, for the two scenarios of nopinone production from CST, direct ozonolysis with consecutive separation, or separation of b-pinene from CST followed by ozonolysis, there is two- to three-times difference in the calculated environmental impacts (acidification potential, human toxicity, fossil depletion and climate change). The reason for this is that in this model, main impacts contributions come from the use of the dilution solvent (ethyl acetate); the amount of solvent is calculated per unit of feed and in two different scenarios the feeds contain different concentrations of the com-

pound of interest (b-pinene). Thus, in the case of prior separation of b-pinene from CST the feed is almost pure b-pinene and productivity is higher than in case of direct ozonolysis, while the amount of dilution solvent stays the same. Impacts are calculated per functional unit, which in our case is the production of 1 tonne of nopinone (Figure 1.4).

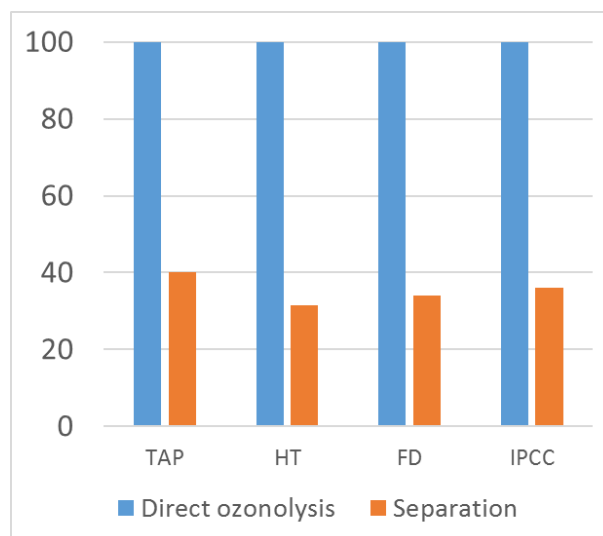


Fig. 1.4: Comparison of environmental impacts from production of nopinone from CST (direct ozonolysis of CST vs separation of b-pinene with following ozonolysis).

Dr Polina YASENEVA

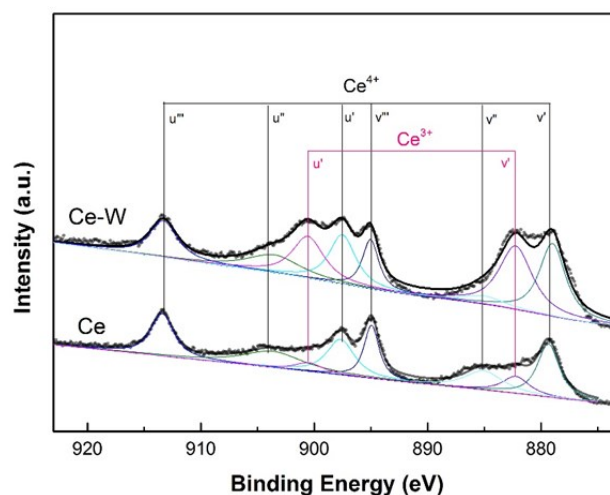
Update on work package 1.3

Novel reactors and process technology

Dr YAN Yong (Research Fellow, NTU) has been working on CO₂ hydrogenation into methanol over Cu based catalysts. To improve the performance of Cu/CeO₂ catalysts, different dopants were investigated. The addition of W promoted the formation of surface oxygen vacancies, which play pivotal roles in activation of CO₂ species. The as-prepared W-CuCe catalysts demonstrated an 8-fold CO₂ conversion rate if compared to the

Fig. 1.5: High-resolution deconvoluted XPS spectra for Ce3d, showing that the W modification enhanced the ratio of Ce³⁺/Ce⁴⁺.

Dr YAN Yong



parent catalysts. Furthermore, the optimal selectivity to CH_3OH has increased from ~ 50 to $\sim 86\%$ by W doping, which could be attributed to the fine-tuning of the adsorption strength and the reactivity of key reaction intermediates. Besides the modification of supports for Cu-based catalysts, Dr Yan tried to control the structure of active sites by pairing Cu nanoparticles with noble metal atoms.

Nicholas JOSE (Research Assistant, CARES) filed a full patent application for the annular microreactor process in February 2019. The method for synthesising and controlling the formation of 2D MOF materials was included in this patent application to gain provisional protection. This manuscript is in the process of being submitted. Work this year will demonstrate the improved performance of these materials in adsorption and catalytic applications.

Building upon the success of initial experiments in mid-2018, LDH electrodes with high specific capacitance and stability were fabricated using a new methodology based on microreactor synthesis and solvent-mediated assembly on substrates. The commercial applicability of these materials is

currently being evaluated.

A room temperature process was developed for the synthesis of carbon quantum dots. High resolution scanning transmission electron microscopy showed that these particles are produced with high precision (3 ± 0.3 nm in diameter). Work continues in the characterisation and purification of quantum dots, with an eye on their utilisation in electrochemistry, catalysis and optical materials.

New work has begun on a recently awarded project (Rapid Industrialisation of Next Generation Nanomaterials – RINGs) under the SMART Innovation Centre. The objective of this project is to develop an accelerated commercial platform for nanomaterial development, which will be used to found a service company for the bespoke nanomanufacturing. To showcase this platform, the team is collaborating with A*STAR to develop ZnO nanoparticle antimicrobial coatings.

Prerna GOYAL's (PhD Student, NUS) research project aims to study drying of wet flue gas by Vacuum Swing Adsorption (VSA) on silica gel adsorbent. Binary breakthrough experiments are conducted for CO_2/N_2 mixture on silica gel over



Prerna GOYAL works on the Vacuum Swing Adsorption pilot plant rig.

a range of process conditions to confirm the mixture equilibrium for these gases. The two-component simulation code is extended to three-component code and simulations for binary breakthrough runs are carried out using the three-component code. A parametric simulation study is undertaken to identify the optimum experimental operating conditions for establishing mixture equilibrium of N_2 in CO_2/N_2 mixture in silica gel. Binary mixture equilibrium of CO_2/N_2 on silica gel is well captured by the single component Langmuir isotherm model. N_2 transport is governed by Knudsen flow and CO_2 transport by a combination of Knudsen and surface flow in a $N_2:CO_2$ mixture in silica gel pores.

Breakthrough experiments are conducted to establish the equilibrium for moisture adsorption and desorption on silica gel and identify its transport mechanism in the pores. Breakthrough experiments for understanding competitive adsorption of CO_2 , N_2 and moisture are conducted. The equilibrium data for moisture adsorption on silica gel is fitted to an isotherm model. The subsequent work activity involves establishing the equilibrium and transport of pure moisture and a ternary mixture (CO_2/N_2 /moisture) adsorption on silica gel.

Jijiang HUANG (PhD student, NTU) submitted his PhD thesis in January 2019 with the title 'Development of Ni-based redox catalysts for chemical looping processes'. In the period of November 2018 to March 2019, he also worked on the dry reforming project to understand the origin of the excellent catalytic performance of the prepared Ni catalysts.

JIA Chunmiao (PhD student, NTU) submitted her PhD thesis in January 2019 with the title 'Model analysis and catalysts study of CO_2 methanation in fluidized bed reactor'. During November 2018 to March 2019, she mainly focused on the thesis manuscript. Chunmiao has finished her research work as a PhD student in C4T and now is working as a Research Assistant in the NTU Singapore-CEA Alliance for Research in Circular Economy (NTU SCARCE).

Bowen LI (PhD student, NUS) is looking at the synthesis of Stöber silica spheres and mesoporous silica structures, which has been long explored in catalysis, since this type of silica is one of the most commonly used catalyst support systems. Furthermore, synthesis of periodic mesoporous organosilicas (PMOs) was independently noted in 1999 by three groups (Ozin and coworkers, Inagaki et al. and Stein and coworkers). While

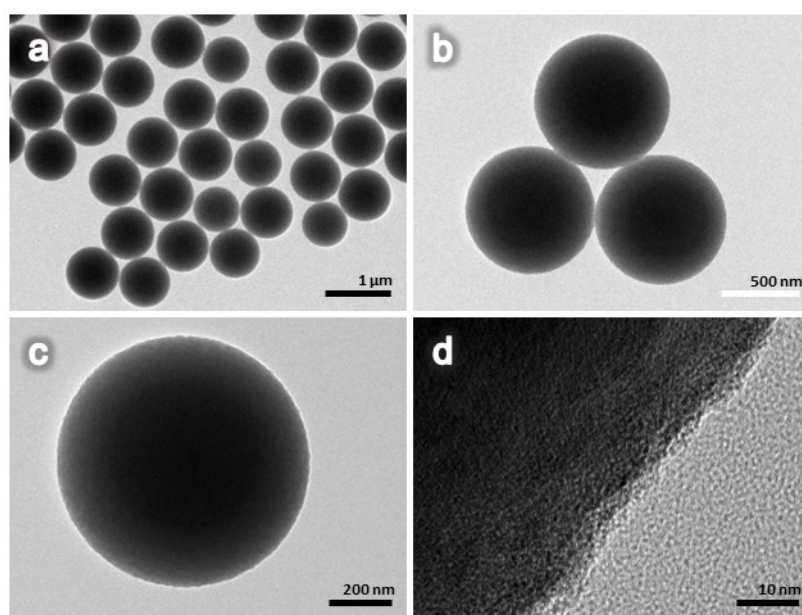


Fig. 1.6: TEM images of PT incorporated MPTMS spheres.

Bowen LI

retaining the advantages of inorganic mesoporous silica structure (high specific surface areas, large pore volume, tunable pore structure, etc.), this organic-inorganic hybrid structure offers distinct advantages by its homogeneously and covalently incorporated organic functional groups. In general, synthesis of PMOs relies on the use of bissilylated organosilica precursors $((R'O)_3Si-R-Si(R'O)_3)$ with R being the bridging organic group. The group has previously proved the synthesis of non-porous organosilica spheres can be done using non-bridged organosilica precursor. As an example, organosilica spheres in sub-micrometer range have been synthesised from 3-mercaptopropyltrimethoxysilane $(R-Si(R'O)_3)$. In the proposed bilayer structure of this organosilica sphere, the organic functional group R is exposed in both ends as compared to PMOs where the R group is imbedded in the silica matrix.

Other research

Automated chemical routes

Dr GUO Zhen (Senior Research Fellow, CARES), with guidance from Prof. Alexei LAPKIN (PI, CAM) has been working on an industrial project in collaboration with BASF. In line with the general objectives of IRP1 as well as Intra-CREATE project eCO₂EP, the goal of this work is to discover new sustainable chemical routes to replace current industrial routes which rely heavily on the oil industry. In contrast to a conventional human-based searching strategy, the screening of chemical routes is automated by data mining reaction databases accumulated over the past 100 years. Given a target compound, relevant data are extracted from the database and traversed into a reaction network. Then, millions of reaction paths are examined based on graph theory and heuristic criteria that are proposed in light of chemical knowledge and industrial requirements. Dr Guo spent one month in Cambridge to bring this technique developed in Prof. Lapkin's group to CARES in Singapore. Preliminary chemical routing has been started and several interesting findings have emerged.

Over the last half year, Bowen and his research colleagues have explored the possibilities of utilising such exposed R groups (thiol group, in this case) to localise metals so that these organosilica spheres could function as a catalyst support. As expected, they could absorb different metal ions by one-pot or stepwise treatments. Noble metals could be introduced by simple mixing in an oil bath while transition metals could be incorporated under hydrothermal conditions. As surveyed by XPS study, most of the incorporated metals remained in their ionic state, which is probably due to the stabilising abilities of the thiolate group. Incorporation of different metals could be carried out together or separately, giving rise to numerous kinds of bimetallic, trimetallic and more complex catalyst compositions. In view of catalyst applications, we have also managed to increase specific surface area of this catalyst by introducing surfactants during synthesis.

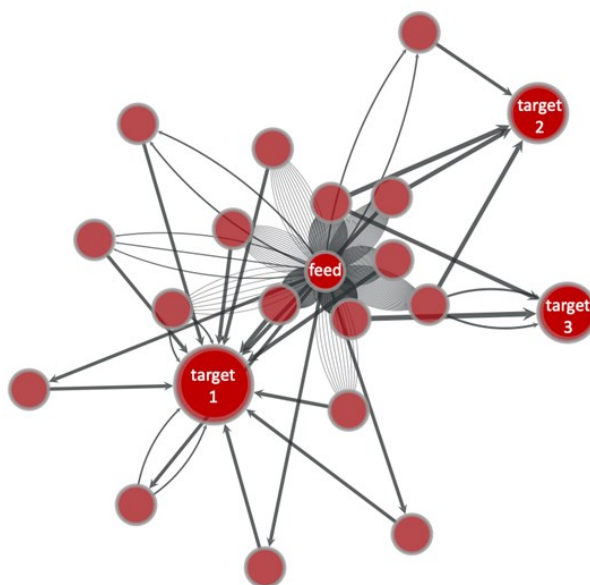


Fig. 1.7: An example of a simple reaction network illustrating the strategy for automated reaction routes search.

Dr GUO Zhen

Scientific output

The following are the CREATE-acknowledged publications generated by IRP1 during the reporting period, excluding those already featured in the Scientific Highlights section on page 13.

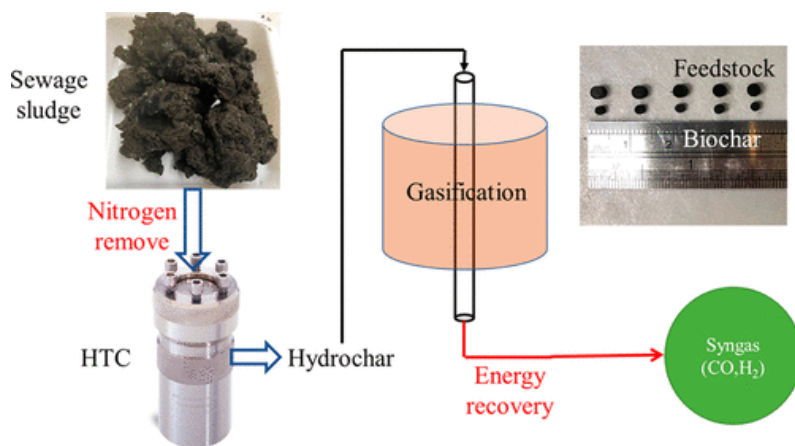
Nitrogen removal and energy recovery from sewage sludge by combined hydrothermal pretreatment and CO₂ gasification

Ye Shen, Chao He, Xiaoping Chen, Alexei A. Lapkin, Wende Xiao and Chi-Hwa Wang, *ACS Sustainable Chemistry & Engineering*

DOI: 10.1021/acssuschemeng.8b03857

Abstract: Disposal of nitrogen-containing sewage sludge (SS) via gasification leads to the formation of NO_x precursors and NO_x and ammonia emissions. Pretreatment of SS via hydrothermal carbonisation (HTC) was shown to improve coalification, desulfurisation, and deamination. In this study, we propose a combined hydrothermal pretreatment and CO₂ gasification process for removal of nitrogen from SS and production of energy via the gasification of the pretreated SS. In the HTC process, around 50% of nitrogen contained in the sludge was removed. The derived hydrochar (HC) was subsequently fed for gasification using CO₂ as a gasifying agent, which was characterised by the expected reduction in the formation of

ammonia. We further improved the process by establishing cogasification of hydrochar with waste leaves. The improvement is believed to be due to the catalytic effect of Ca, present in plant leaves, on the gasification. Cold gas efficiency of the cogasification process of a 1/1 hydrochar/leaves blend by mass was enhanced to 66%. The combination of hydrothermal conversion of sewage sludge with CO₂ cogasification of hydrochar and waste leaves was shown to be a clean and efficient method for SS management and energy recovery.



Influence of hydrodynamics on wet syntheses of nanomaterials (book section)

Nicholas Jose and Alexei Lapkin, *Advanced Nanomaterials for Catalysis and Industry*

DOI: 10.1016/B978-0-12-814807-5.00002-4

Abstract: The industrial-scale production of structured nanomaterials is a significant challenge due to typically low throughputs, high operating costs of manufacturing, and difficulties in maintaining consistent product quality. Understanding the effects of hydrodynamics on the colloidal synthesis of nanomaterials is crucial to our ability to rationally develop scalable processes, which would accelerate the traditionally slow, heuristic scale-up efforts. In this chapter, we review the effects of

hydrodynamics from the macroscale to the molecular scale. At the macroscopic scale, hydrodynamics governs mixing, which in turn controls particle size and uniformity. At the mesoscopic scale, hydrodynamics governs particle interactions, such as aggregation, ordering, and breakup. At the molecular scale, hydrodynamic shear can influence nucleation, crystallisation, and polymorphism in certain systems, which is hypothesized in recent studies to be through the manipulation of prenucleation clusters. By reviewing relevant theory and experimental studies, we show how to estimate proper reactor and operating conditions using characteristic timescales.

Origins of complex solvent effects on chemical reactivity and computational tools to investigate them: a review

Jithin John Varghese and Samir Mushrif, *Reaction Chemistry & Engineering*

DOI: 10.1039/C8RE00226F

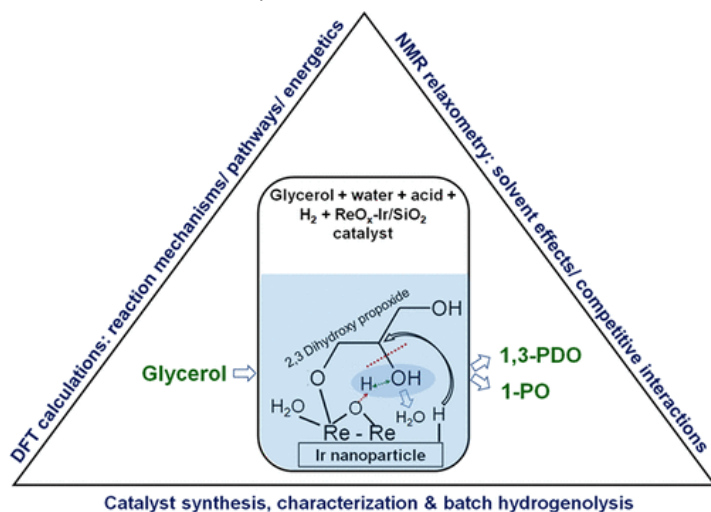
Abstract: Solvents are crucial components in specialty chemical and pharmaceutical industries and in electrochemical and photoelectrochemical processes, and are increasingly being used in catalytic reactions. Solvents significantly influence the kinetics and thermodynamics of reactions and can alter product selectivity markedly. While such solvent effects are observed routinely, identification of the root causes of such effects is less frequent. Solvents can influence reaction rates, conversion and product selectivity by 1) directly participating in the reaction steps and opening alternate reaction pathways, 2) competing with the reactant for interaction with the catalysts, 3) changing the relative stabilization of the reactant, the transition state (TS) and/or the product, 4) altering intra-pore diffusion characteristics in po-

rous catalysts, 5) exhibiting entropic confinement effects altering free energy barriers of reactions, 6) changing the solubility of different components in the reaction mixture, and 7) inhibiting undesired reactions. Their indirect influences may be due to 1) changes brought on to active sites on catalysts and 2) altered structure/stability of catalysts. This article discusses these fundamental reasons behind observed solvent effects with suitable examples. Advances in computational chemistry have led to the development of multiple tools and techniques, considering solvents either as implicit or as explicit molecules, providing molecular insights into complex solvent effects in catalysis. This article provides an overview of some of these methods with suitable examples to demonstrate their application and potential. This mapping of the solvent effects and their origins is believed to aid in the rational selection of solvents for catalytic reactions. The description of the computational tools, their application and their potential is likely to encourage widespread use of these techniques to investigate solvent effects.

Synergistic contribution of the acidic metal oxide-metal couple and solvent environment in the selective hydrogenolysis of glycerol: a combined experimental and computational study using ReO_x-Ir as the catalyst

Jithin John Varghese, Liwei Cao, Christopher Robertson, Yanhui Yang, Lynn F. Gladden, Alexei A. Lapkin and Samir Mushrif, *ACS Catalysis*

DOI: 10.1021/acscatal.8b03079



Abstract: Comprehensive mechanistic insights into the aqueous-phase hydrogenolysis of glycerol by the ReO_x-Ir catalyst were obtained by combining density functional theory (DFT) calculations with batch reaction experiments and detailed characterisation of the catalysts using X-ray diffraction, X-ray photoelectron spectroscopy, and Fourier transform infrared techniques. The role and contribution of the aqueous acidic reaction medium were investigated using NMR relaxometry studies complemented with molecular dynamics and DFT calculations. At higher glycerol concentration, the enhanced competitive interaction of glycerol with the catalyst improved the conversion of glycerol. Sulfuric acid increased the concentration of glycerol within the pores of the catalyst and enhanced the propensity for dissociative adsorption of glycerol on the catalyst, explaining the promotional effect of acid during hydrogenolysis. Partially reduced and dispersed Brønsted acidic ReO_x clusters on metallic Ir nanoparticles facilitated dissociative attachment of glycerol and preferential formation of the primary propoxide. The formation of the dominant

product, 1,3-propanediol (1,3-PDO), results from the selective removal of the secondary hydroxyl of glycerol, with a comparatively low activation barrier of $123.3 \text{ kJ mol}^{-1}$ in the solid Brønsted acid-catalyzed protonation–dehydration mechanism or $165.2 \text{ kJ mol}^{-1}$ in the direct dehydroxylation mechanism. The formation of 1-propanol (1-PO) is likely to follow a successive dehydroxylation pathway in the early stages of the reaction. Although 1,3-PDO is less reactive than 1,2-propanediol (1,2-PDO), it preferentially adsorbs on the catalyst in a mixture containing glycerol to

form 1-PO. The thermodynamically favorable pathway involving dehydrogenation, dehydroxylation, and hydrogenation elementary steps led to the dominant production of 1,2-PDO on pure Ir catalyst with a high C–O bond cleavage barrier of $207.4 \text{ kJ mol}^{-1}$. The optimum $\text{ReO}_x\text{-Ir}$ catalyst with an Ir/Re ratio of 1 exploits the synergy of the sites of both the components. The detailed insights presented here would guide the rational selection of catalysts for the hydrogenolysis of polyols and the optimisation of reaction parameters.

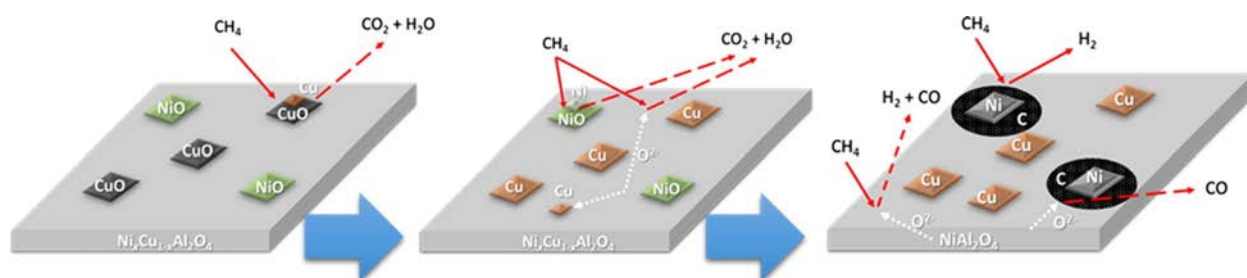
Phase interactions in Ni-Cu- Al_2O_3 mixed oxide oxygen carriers for chemical looping applications

Jijiang Huang, Wen Liu, Wenting Hu, Ian Metcalfe, Yanhui Yang and Bin Liu, *Applied Energy*

DOI: 10.1016/j.apenergy.2018.12.029

Abstract: Chemical looping processes present great potentials to achieve carbon capture and fuel conversion with high thermodynamic efficiencies. Well-known applications of chemical looping include combustion and methane reforming, where phase interactions in oxygen carriers play important roles in determining the process performance. In this study, we systematically investigate the interactions between various phases in Ni-Cu- Al_2O_3 mixed oxides oxygen carriers, which were prepared from layered double hydroxides precursors, synthesised hydrothermally using urea and metal nitrates. It appears that the addition of 32–45 wt% Al_2O_3 was sufficient to prevent sintering effects over 100 redox cycles at

800°C , 1 atm, using methane as the fuel. The oxide phases and their compositions were determined using a set of complementary analytical techniques, allowing us to establish relationships between (i) the compositions of the mixed oxides, (ii) the chemical activity of the various types of lattice oxygen present and (iii) the distributions of gaseous products of chemical looping methane oxidation. We found that the mutual doping between NiO and CuO leads to enhanced lattice oxygen activities, whilst the solid solution of NiAl_2O_4 and CuAl_2O_4 leads to reduced lattice oxygen activity in the spinel phase, which also turns out to be particularly resistant to carbon deposition. The generality of the composition – activity – performance relationship is demonstrated by the successful prediction of the product distributions of methane oxidation based on solely the elemental compositions of the oxygen carriers. These findings enable the rational formulation of Ni-Cu- Al_2O_3 oxygen carriers for methane conversion with precise control of product selectivity.



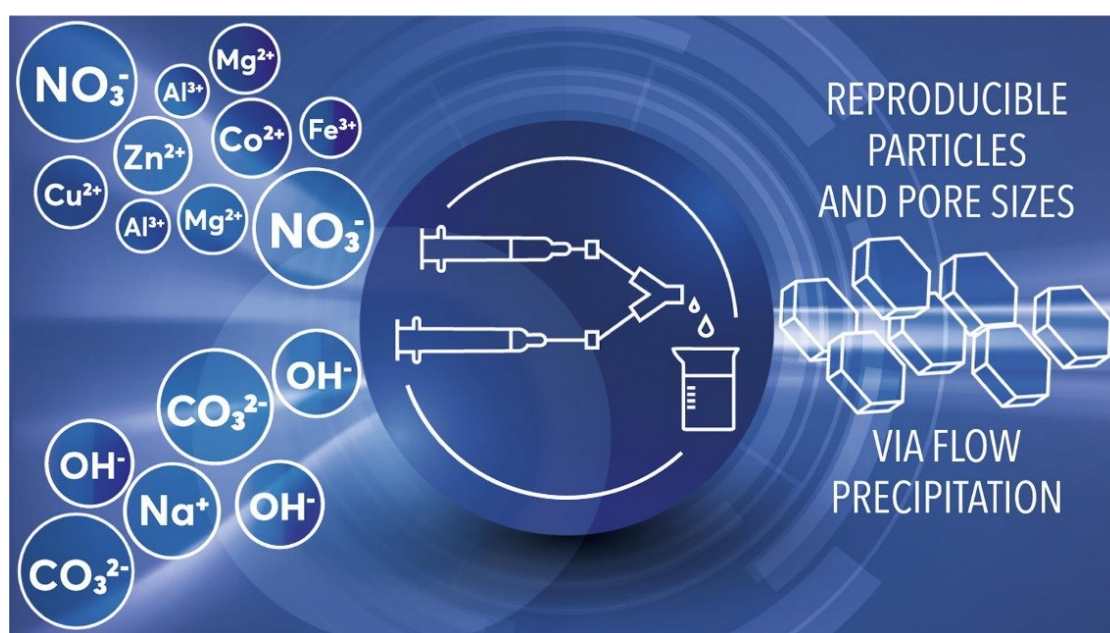
Continuous synthesis of doped layered double hydroxides in a meso-scale flow reactor

Polina Yaseneva, Nan An, Matt Finn, Nicholas Tidemann, Nicholas Jose, Adelina Voutchkova-Kostal and Alexei A. Lapkin, *Chemical Engineering Journal*

DOI: 10.1016/j.cej.2018.11.197

Abstract: Layered double hydroxides are a class of low-cost structured nanomaterials with many potential applications in environmental catalysis and sustainable technologies. Their large-scale use is hindered by the challenge of *reproducible* synthesis at scale. Here we report a general, readily scalable process for the reproducible synthesis of transition metal doped hydrotalcites using a two-step process: co-precipitation in a mm-scale (meso-scale) continuous flow reactor, followed by aging. We have shown that co-precipitation in

flow at a residence time close to the micromixing time affords good control of particle formation. Reproducible synthesis allowed us, for the first time, to investigate the formation of the pore morphology of hydrotalcites and their thermal stability as a function of metal doping. The obtained samples exhibited surface areas ($80\text{--}150\text{ m}^2\text{ g}^{-1}$) higher than those typically attained in batch syntheses, with very low standard deviation between the samples, a high degree of crystallinity and small crystallite sizes, in the range of $9.5\text{--}11.9\text{ nm}$, depending on composition. A systematic characterization allowed us to elucidate the mechanism of the pore morphology formation: the crystallites were found to agglomerate into disk-like platelets, whereas the pore structure of the hydrotalcites is formed by agglomeration of the platelets.



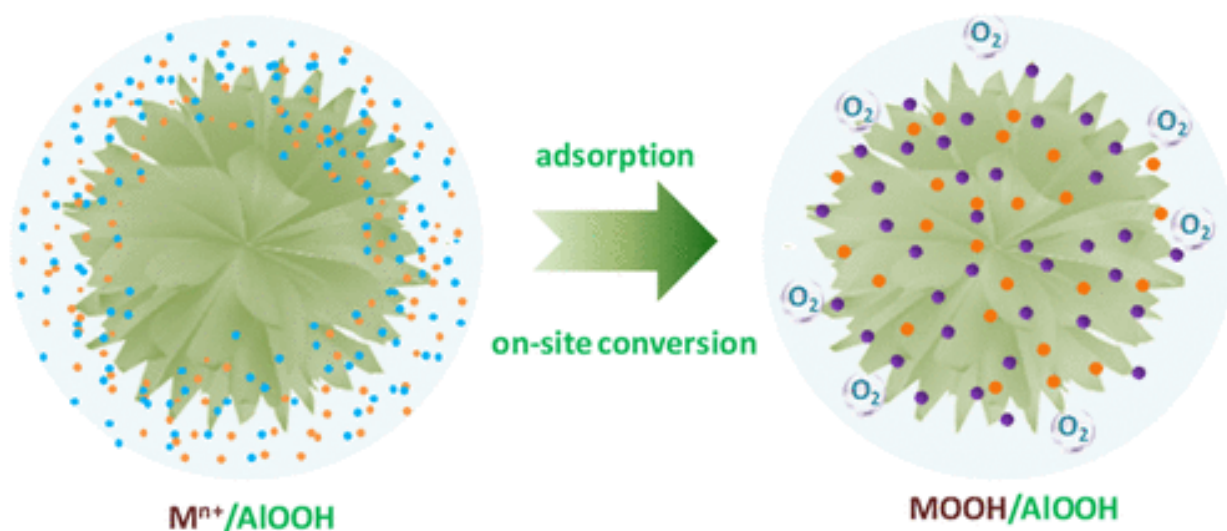
Adsorption and on-site transformation of transition metal cations on Ni-doped AlOOH nanoflowers for OER electrocatalysis

Yao Zhou and Hua Chun Zeng, *ACS Sustainable Chemistry & Engineering*

DOI: 10.1021/acssuschemeng.8b06020

Abstract: AlOOH has long been used as excellent adsorbent for removal of heavy metal cations from wastewater. Herein we report one-pot synthesis of carboxylic-functionalised Ni-doped AlOOH nanoflowers (AlOOH NFs) with high adsorptive capability toward various transition metal cations, and more importantly, the AlOOH NFs adsorbed with various transition metal cations were for the first time directly used as electrocatalyst for oxygen evolution reaction (OER). By simply manipulating the initial metal cation concentration and their molar ratio, the OER cata-

lytic performance of the resulting catalysts could be modulated. The lowest overpotential at a current density of 10 mA cm^{-2} prepared from AlOOH NFs adsorbed with Fe^{III} and Ni^{II} is 0.32 V in 0.1 M KOH and 0.275 V in 1.0 M KOH. Such AlOOH-supported electrocatalyst demonstrates remarkable stability, which shows no evident increase of the overpotential at 10 mA cm^{-2} after 2 h of steady electrolysis at an overpotential of 0.42 V. The excellent OER electrocatalytic activity originates from the on-site formation of ultrafine FeOOH and NiOOH nanoclusters with average sizes below 3 nm during the electrocatalytic process. As such, we demonstrate the workability of using functionalised AlOOH NFs as a bifunctional platform for adsorption of transition metal cations and easy preparation of efficient and cost-effective OER catalysts.

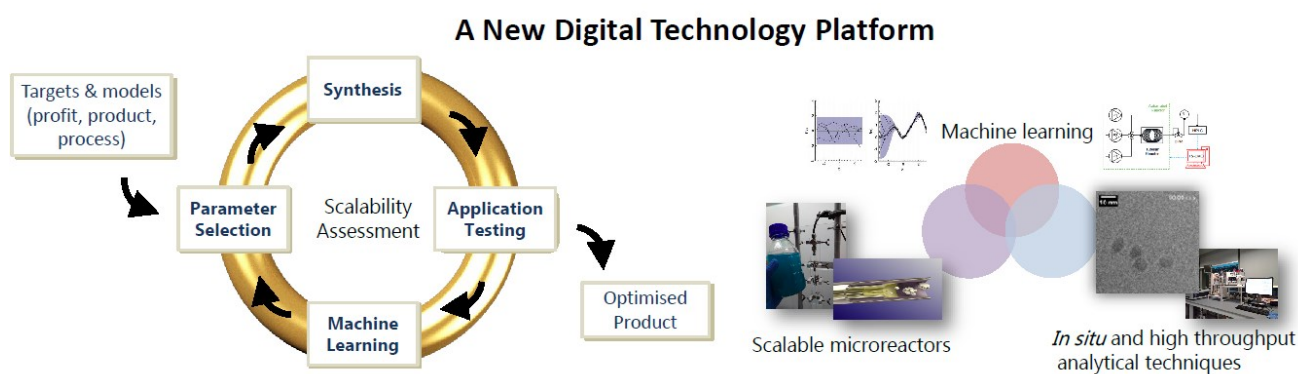


Other activities and achievements

PhD student Liwei CAO (CAM) won the Best Presentation Award at the 2018 Network of Asian Open Research Family Day in Shanghai in November. In close collaboration with BASF scientists, Liwei has built up a machine learning algorithm for the prediction of personal care formulation performance. Liwei's thesis title is 'Combining artificial intelligence and automated experimental platform in formulated product design'.

New work has begun on the recently awarded project (*Rapid Industrialisation of Next Generation Nanomaterials – RINGs*) under the SMART Innovation Centre, led by **Research Assistant Nicholas JOSE (CARES)**. The objective of this project is to develop an accelerated commercial platform for nanomaterial development, which will be used to found a service company for the bespoke nanomanufacturing. To showcase this platform, researchers are collaborating with A*STAR to develop ZnO nanoparticle antimicrobial coatings.

RINGs abstract: Nanostructured materials have growing value in many applications, from energy storage to biomedicine. However, many companies struggle to commercialise nanomaterial-based products due to lengthy development times (up to 10-30 years) and the technical difficulties of scaling up. We use a disruptive methodology for R&D and manufacturing that integrates scalable microreactor technologies with machine learning, automated laboratories and high-throughput analysis. In our proof of concept demonstration, we will rapidly develop a process for the scalable manufacture of antimicrobial zinc oxide coatings.





IRP2

ELECTROSYNTHETIC PATHWAYS FOR ADVANCED LOW-CARBON CHEMICAL MANUFACTURING

In IRP2, low carbon electrosynthetic processes and technologies are developed which target local, on-scale and on-demand conversion of electricity to commodity or specialty chemicals. As the contribution of renewables to the total electricity generation capacity continues to grow, novel technological opportunities arise for direct chemical conversion of the newly available low carbon electrons. This project addresses core challenges to the implementation of low carbon, on-demand driven advanced manufacturing of chemical targets via electrosynthesis.

IRP2 Principal Investigators:



Dr Adrian FISHER
University of Cambridge



Professor WANG Xin
Nanyang Technological University



Professor LEE Jim Yang
National University of Singapore



OVERVIEW

In the latest reporting period, IRP2 researcher Dr Kamal ELOUARZAKI (Senior Research Fellow, NTU), has demonstrated a unique example of a chemical inactivation/redox activation process (IAP) based on a non-enzymatic catalyst prepared by mixing rhodium-porphyrinic catalyst and an interconnected multi-walled carbon nanotubes matrix which presents an excellent and stable electron transfer. Electrochemistry, mathematical models and DFT calculations were combined to uncover the molecular IAP at the catalytic metallic site. These findings offer novel perspectives for the design of finely optimised catalysts by eliminating the inactivation phenomena and could eventually be decisive in the quest to elucidate the complexity of hydrogenase electrochemical results.

In a further development, Dr Elouarzaki has co-founded a new startup company Datum Electronix with Dr Adrian FISHER (PI, University of Cambridge). The company has been formed to explore commercial openings focused on opportunities from the ongoing convergence of the electronic and chemical industries.

In collaboration with Prof. Xu ZHICHUAN (Co-I, NTU), Dr Chencheng DAI (Research Fellow, NTU) has reported advances in heterostructured electrocatalysts for the hydrogen evolution reaction (HER), under alkaline conditions. In industrial water electrolysis, the HER is often conducted in alkaline media to achieve higher stability of the electrode materials. However, the kinetics of the HER in an alkaline medium are slow relative to that in acid because of the low concentration of protons in the former.

In collaboration with Prof. Erik BIRGERSSON (Co-I, NUS), Dr Kuppa Ashoke RAMAN (Research Fellow, NUS) and Vishvak KANNAN (PhD student, NUS) work has continued in the area of advanced numerical analysis. In this reporting period, the development of strategies for the sensitivity analysis of a galvanic electrochemical reactor (ECR) is presented. The galvanic ECR is operated potentiostatically and is investigated at different operating potentials. The mechanistic mathematical models developed for this ECR were subjected to Monte Carlo Simulations (MCS) in order to perform the sensitivity analysis. The results will be used to support the development of cells for the micro-variable pressure and temperature electrosynthesis plant, and more broadly, the design of next generation electrochemical reactors.

In collaboration with Prof. Jim Yang LEE (PI, NUS), Shengliang ZHANG (PhD student, NUS) is studying dual-band electrochromic smart windows with independent control of near-infrared and visible light transmittance. His most recent work was focused on addressing the technical challenges of a new variant of electrochromic energy storage (EES) windows. Shengliang circumvented current technical issues by modifying an Al anode with surface pre-lithiation; and demonstrated the viability of this strategy with the design of a new, electrically rechargeable dual-band electrochromic energy storage (DBEES) window.

The development of the IRP2 international outreach programme has continued with the delivery of a new programme on Fourier transform and ac methods in collaboration with Metrohm and Monash University in Melbourne. The mas-

terclass programme was delivered by Dr Fisher and Professor Alan BOND (Monash), highlighting the potential of advanced FFT strategies in electrochemical analysis. The next programme is scheduled for Singapore in June 2019.

Dr Adrian Fisher, PI
University of Cambridge

Update on work package 2.1

Advanced electrode architectures

Dr Kamal ELOUARZAKI (Senior Research Fellow, NTU) reports that in response to issues raised by modern energy challenges, molecular electrocatalysis is currently attracting a lot of attention to the tailoring of “model” catalysts – notably understanding the mechanisms, kinetic and thermodynamic parameters that occur during a catalytic reaction. In this regard, nature offers extremely efficient enzymes called hydrogenases. These enzymes, which catalyse the reversible interconversions between H_2 and H^+ at high turnover rates, are inactivated by O_2 . This inactivation yields odd cyclic voltammetric responses originating from a chemical inactivation/redox activation process (IAP). Although IAP has been extensively studied for hydrogenases, their catalytic mechanism is not fully understood because of the intricate but necessary electrical wiring, desorption and complex biochemical environment required. Here, Dr Elouarzaki reports a unique example of IAP based on a non-enzymatic catalyst prepared by mixing rhodium-porphyrinic catalyst and an interconnected multi-walled carbon nanotubes matrix which presents an excellent and stable electron transfer. Electrochemistry, mathematical models and DFT calculations were combined to uncover the molecular IAP at the catalytic metallic site. A mechanistic analysis of the non-catalytic and catalytic responses exhibited by this complex is presented, enabling a comprehensive understanding of the thermodynamic and kinetic parameters that gov-

ern the IAP. These stepwise studies support a mechanism for glucose oxidation that proceeds through an EC'CE scheme with catalytic steps similar to the ones reported for hydrogenases. The overall mechanism of the molecular IAP was detailed based on experimentally validated models and compared to hydrogenase IAP. These findings offer novel perspectives to design finely optimised catalysts by eliminating the inactivation phenomena and could eventually be decisive in the quest to elucidate the complexity of hydrogenase electrochemical results.

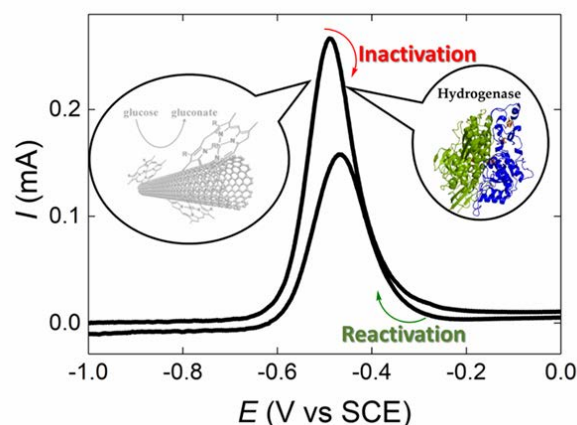


Fig. 2.1: Hydrogenase-like electrocatalytic activation and inactivation mechanism by three-dimensional binder-less molecular catalyst.

Dr Kamal ELOUARZAKI

Dr Chencheng DAI (Research Fellow, NTU)

Heterostructured Electrocatalysts for Hydrogen Evolution Reaction Under Alkaline Conditions. The hydrogen evolution reaction (HER) is a half-cell reaction in water electrolysis for producing hydrogen gas. In industrial water electrolysis, the HER is often conducted in alkaline media to achieve higher stability of the electrode materials. However, the kinetics of the HER in an alkaline medium are slow relative to that in acid because of the low concentration of protons in the former. Under the latter's conditions, the entire HER process will require additional effort to obtain protons by water dissociation near or on the catalyst surface. Heterostructured catalysts, with fascinating synergistic effects derived from their heterogeneous interfaces, can provide multiple functional sites for the overall reaction process. At present, the activity of the most active known heterostructured catalysts surpasses (platinum-based heterostructures) or approaches (noble-metal-free heterostructures) that of the commercial Pt/C catalyst under alkaline conditions, demonstrating an infusive potential to break through the bottlenecks. This review summarises the most representative and recent heterostructured HER catalysts for alkaline medium. The basics and principles of the HER under alkaline conditions are first introduced, followed by a discussion of the latest advances in heterostructured catalysts with/without noble-metal-based heterostructures. Special focus is placed on approaches for enhancing the reaction rate by accelerating the Volmer step. This review aims to provide an overview of the current developments in alkaline HER catalysts, as well as the design principles for the future development of heterostructured nano- or micro-sized electrocatalysts.

Recommended Practices and Benchmark Activity for

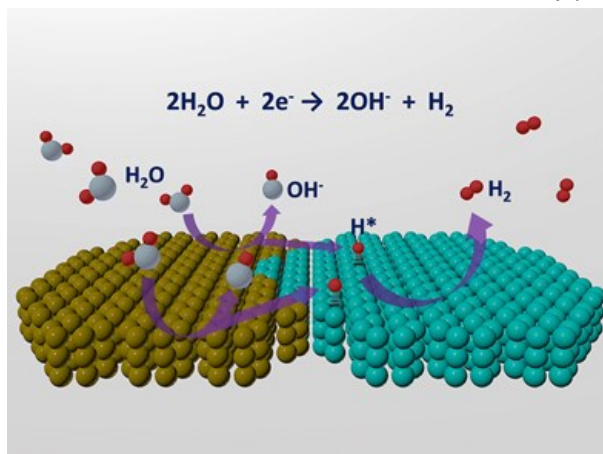


Fig. 2.2: Mechanism of hydrogen evolution reaction on heterostructure electrocatalysts under alkaline conditions.

Hydrogen and Oxygen Electrocatalysis in Water Splitting and Fuel Cells. Electrochemical energy storage by making H₂ an energy carrier from water splitting relies on four elementary reactions, i.e., the hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Herein, the central objective is to recommend systematic protocols for activity measurements of these four reactions and benchmark activities for comparison, which is critical to facilitate the research and development of catalysts with high activity and stability. Details for the electrochemical cell setup, measurements and data analysis used to quantify the kinetics of the HER, HOR, OER and ORR in acidic and basic solutions are provided, and examples of state-of-the-art specific and mass activity of catalysts to date are given. First, the experimental setup is discussed to provide common guidelines for these reactions, including the cell design, reference electrode selection, counter electrode concerns and working electrode preparation. Second, experimental protocols, including data collection and processing such as ohmic- and background-correction and catalyst surface area estimation, and practice for testing and comparing different classes of catalysts are recommended. Lastly, the specific and mass activities of some state-of-the-art catalysts are benchmarked to facilitate the comparison of catalyst activity for these four reactions across different laboratories.

Accompanying figure >

Exceptionally active iridium evolved from a pseudocubic perovskite for oxygen evolution in acid. Exploring robust catalysts for water oxidation in acidic electrolyte is challenging due to the limited material choice. Iridium (Ir) is the only active element with a high resistance to the acid corrosion during water electrolysis. However, Ir is rare, and its large-scale application could only be possible if the intrinsic activity of Ir could be greatly enhanced. Here, a pseudo-cubic $\text{SrCo}_{0.9}\text{Ir}_{0.1}\text{O}_{3-\delta}$ perovskite, containing corner-shared IrO_6 octahedrons, is designed. The Ir in the $\text{SrCo}_{0.9}\text{Ir}_{0.1}\text{O}_{3-\delta}$ catalyst shows an extremely high intrinsic activity as reflected from its high turnover frequency,

which is more than two orders of magnitude higher than that of IrO_2 . During the electrochemical cycling a surface reconstruction, with Sr and Co leaching, over $\text{SrCo}_{0.9}\text{Ir}_{0.1}\text{O}_{3-\delta}$ occurs. Such a reconstructed surface region likely contains a high amount of structural domains with corner-shared and under-coordinated IrO_x octahedrons, and is responsible for the observed high activity.

Fig. 2.4: A schematic that illustrates the surface reconstruction over the $\text{SrCo}_{0.9}\text{Ir}_{0.1}\text{O}_{3-\delta}$ surface.

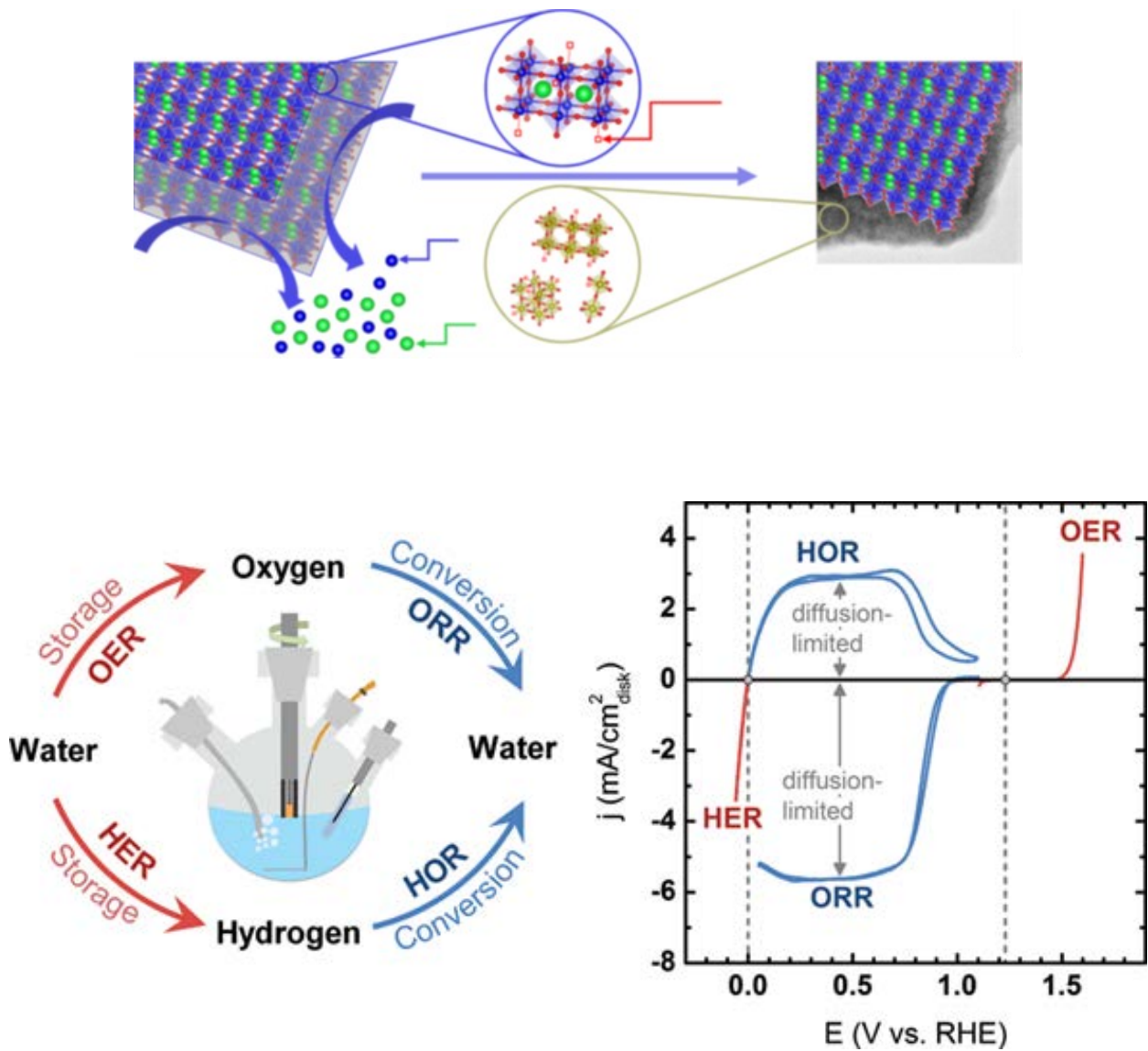


Fig. 2.3: The rigorous protocols for activity measurements are the prerequisite of developing highly active electrocatalysts for water splitting and hydrogen fuel cell reactions.

Selective Electro-reduction of Carbon Dioxide to Formic Acid on Cobalt-Decorated Copper Thin Films. The development of highly efficient, selective and economic approaches for electrochemical reduction of carbon dioxide to hydrocarbons is a promising way to promote the sustainable carbon cycle nowadays. Here, we report a stable cobalt-decorated copper catalyst with significantly enhanced selectivity towards formic acid produced from CO₂ through electrochemical reduction. This catalyst was prepared through the electro-deposition of cobalt on the surface of copper, followed by Ar and air atmosphere treatment. The

as-prepared catalyst exhibits selective conversion of CO₂ to formic acid with a Faradaic efficiency of ca. 80% at applied potential of -0.65 V vs. reversible hydrogen electrode. Meanwhile, the copper electrode treated with the same condition without cobalt decoration and the cobalt-decorated copper electrode without Ar treatment process only show a FE towards formic acid of ca. 56% and ca. 57% from CO₂ reduction, respectively. This study represents a facile decoration method to prepare highly selective electrocatalyst for the efficient reduction of CO₂ to value-added chemicals in aqueous electrolyte.

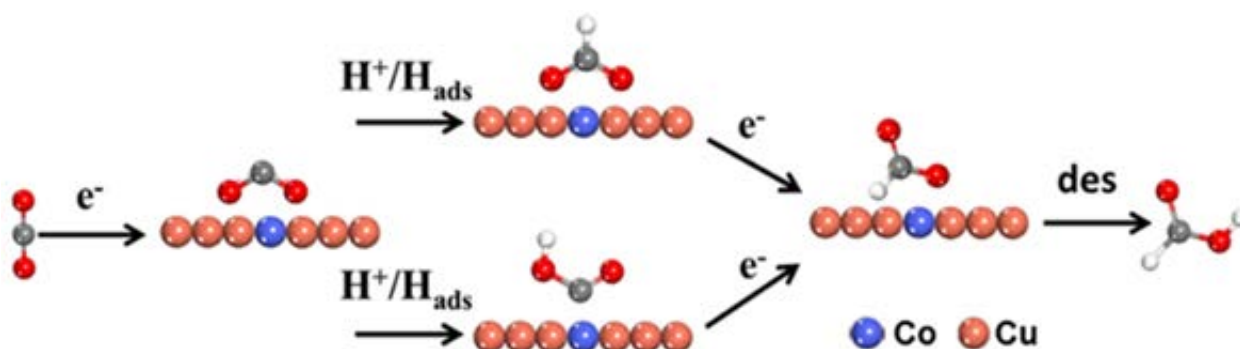


Fig. 2.5: Proposed mechanism for the electrochemical reduction of CO₂ to formic acid on CuCo electrode (Red - oxygen; grey - carbon; bronze - copper; blue - cobalt; white - hydrogen).

Dr Chencheng DAI

Nur Farhanah's BTE ROSLI's (PhD student, NTU) recent work investigated the electrochemical properties and applications of MAX and MAB phases. Six MAX and MAB phases (Ti₂AlC, Ti₂AlN, Ti₃AlC₂, Ti₃SiC₂, Cr₂AlB₂ and MoAlB) were successfully synthesised and characterised by SEM, EDS and XPS, XRD and Raman spectroscopy prior to studying their electrochemical and electrocatalytic application. From the results, these materials possess negligible inherent electroactivities and displayed no apparent electrocatalytic properties towards OER. Amazingly, with an exception from Ti₂AlN, MAX and MAB phases possess high HET rates, improved perfor-

mance for ascorbic acid and uric acid detection and displayed enhanced electrocatalytic performance towards HER and ORR. In addition, the materials have near negligible toxicity towards lung, kidney, liver and breast cancer cells. They impose low toxicity towards A549, MCF-7, HEK 293 and HepG2 cells and when compared with literature, they are found to be the most non-toxic group of layered materials thus far. Hence, they can be deemed as safe and promising materials for future sensing and energy applications with potential biocompatibility in humans for future biological applications.

Guo Xiong THAM (PhD student, NTU) is working on the development of a conducting polymer (CP) film with the use of electrochemical polymerisation (ECP) in the cathode or anode. The use of ECP allows for a simple, rapid, stable and selective preparation of certain CP films to be electropolymerised and considered further in applications such as secondary batteries and supercapacitors. The use of aniline and melamine in a strongly acidic medium was investigated with their desired monomeric ratio determined as part of the optimum conditions for electropolymerisation. The use of COOH-functionalised multi

walled carbon nanotubes on the glassy carbon working electrode surface also enhances the strong noncovalent interactions with the electro-co-polymer. Studies on the stability of the electro-co-polymer in a monomer-free solution indicate that the peak current density was halved approximately at the 800th and 90th cycle corresponding to the intertwined chains of polyaniline and polymelamine respectively. More studies are needed to improve the peak current density of the daughter polymeric melamine of the electro-co-polymer.

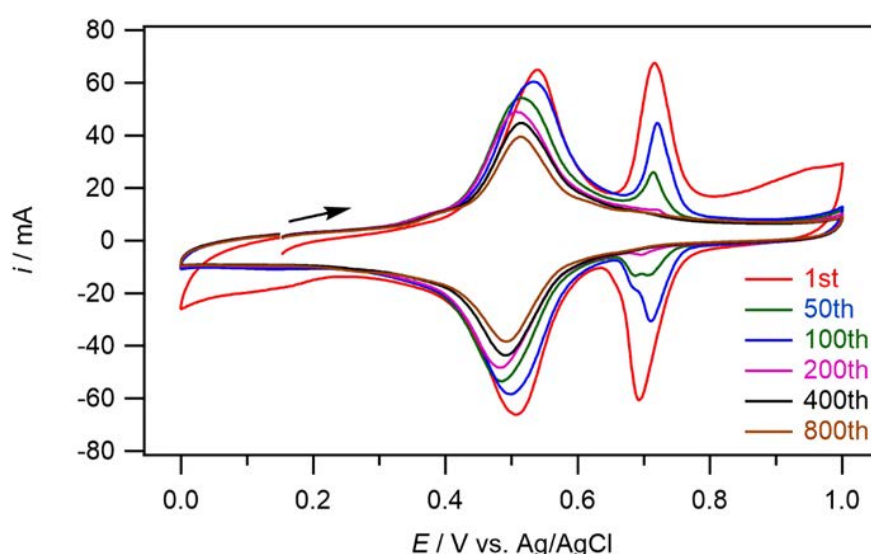


Fig. 2.6: Cyclic voltammograms of the poly (aniline-co-melamine) film on a 3-mm GCE* modified surface in 1.0 M monomer-free HCl solution at a scan rate of 20 mV s⁻¹. The legend depicts the cycle number of the cyclic voltammogram.

Guo Xiong THAM

Update on work package 2.2

Co-generation and electrolytic synthesis reactor engineering

Dr Libo SUN (Research Fellow, NTU) reports that in his previous work, one new N₄ macrocyclic structure was used for preparation of one metal complex, which exhibited high selectivity and activity for CO₂ reduction to CO. The unravelling of structure features suggested that an electronic structure contribution from ligand to metal affects its activity. Theoretical analysis also indicates that the metal complex has a lower energy barrier for the rate determining step-adsorption

of intermediate *COOH during the CO₂ reduction process, and thus enhances CO yielding activity. The performance of metal complex obtained for electrochemical CO₂ conversion in aqueous medium outperformed most of other metal complexes (metal porphyrin or phthalocyanines) reported so far. Following this idea, an attempt was made to develop a catalyst with even lower overpotentials as such similar structures. Thus, a new series of ligands based on similar structures was prepared

and used. From the experimental results, they could indeed exhibit lower overpotential while maintaining high activity and selectivity, at least an overpotential of about 190 mV could be achieved. The work is in progress.

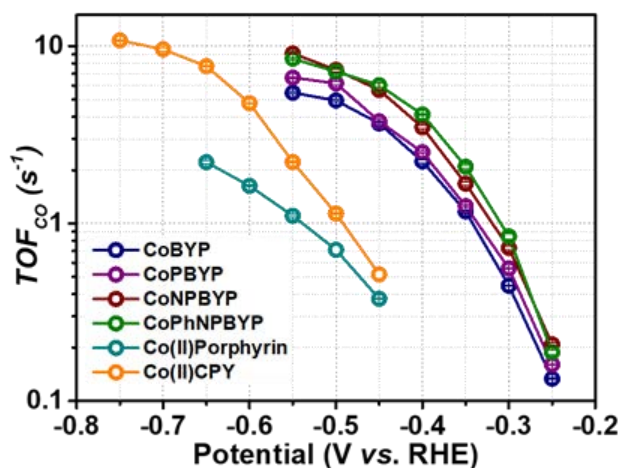


Fig. 2.7: Potential applied versus turnover frequency (TOF) of CO. Co(II)Porphyrin represents the performance of commercial cobalt(II) meso-tetraphenylporphine. Co(II)CPY represents the performance of metal complex prepared in our previous work. All the others, such as CoBYP, CoPBYP, CoNPBYP, CoPhNPBYP are metal complexes prepared in this work. From the figure, it is obvious that the latter metal complexes need lower overpotential to be driven whilst could reach high TOF toward CO yielding. Thus, such a series of catalysts has higher energy utilisation than either Co(II)Porphyrin or Co(II)CPY.

Dr Libo SUN

Dr Tianran ZHANG (Research Fellow, NUS) is strongly interested in the design and synthesis of low-cost electrocatalysts for rechargeable metal-air batteries. Recently, he has developed a new strategy to increase the energy efficiency of quasi-neutral rechargeable Zn-air batteries. Specifically, he coupled Mn redox reactions to the Zn-air battery chemistry by introducing a Mn^{2+} additive into the quasi-neutral electrolyte. The resulting Mn-redox-assisted quasi-neutral Zn-air battery using a phosphate-modified manganese oxide

(PMO) catalyst in the air cathode showed a high round-trip energy efficiency of 53.4%, which could be increased further to 63.2% when the catalyst was upgraded to a PMO-nitrogen doped reduced graphene oxide (RGO) composite. Such performances are on par with the current alkaline rechargeable Zn-air batteries using state-of-the-art non-noble metal catalysts. This study therefore provides a new way of thinking in the design of rechargeable Zn-air batteries for mild electrolytes.

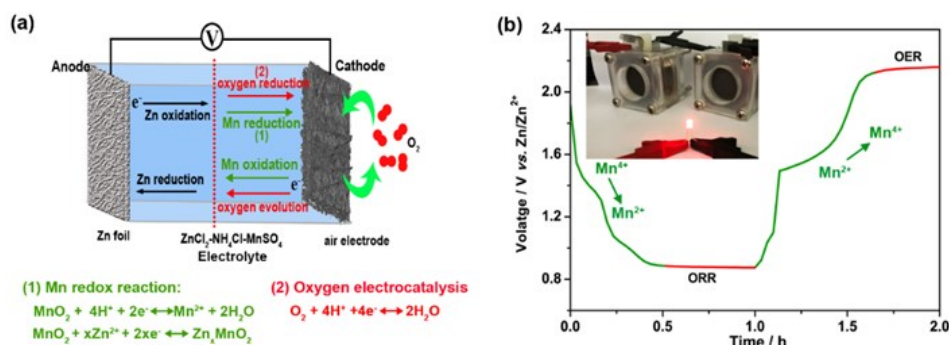


Fig. 2.8: **a** Configuration of the Mn-redox-assisted ZnAB (MRA-ZnAB) with the Mn^{2+} -containing quasi-neutral electrolyte. **b** A typical discharge-charge curve of the MRA-ZnAB. The inset shows two quasi-neutral MRA-ZnABs powering up a light emitting diode.

Dr Tianran ZHANG

Vishvak KANNAN (PhD student, NUS) gives a summary of the progress in the sensitivity analysis of a galvanic electrochemical reactor (ECR).

This galvanic ECR is operated potentiostatically and is investigated at different operating potentials. The mechanistic mathematical models developed for this ECR were subjected to Monte Carlo Simulations (MCS) in order to perform the sensitivity analysis.

In the MCS, Vishvak simultaneously varied over 35 stochastic parameters. The parameter set comprised of samples that are randomly varied following a normal distribution around a prescribed mean and standard deviation. The means were selected from the base case which was validated with experiments and were subjected to a 5% standard deviation to generate the sample space with a sample size of 2500. The performance of the galvanic ECR at different operating potentials corresponding to three different regions of operations - activation loss, ohmic loss and mass transport limited regions - were studied. The results are presented in the figure below. The current has a linear relationship to the applied cell potential only in the ohmic loss region. Additionally, the standard deviation of the performance is the largest in the activation loss region which

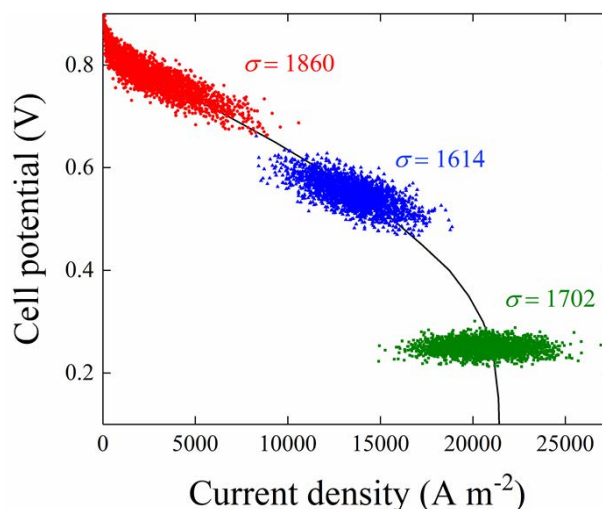
Fig. 2.9: Cell performance vs the applied cell potential. The solid line (—) represents the base case polarisation curve and the red circles (●), blue triangles (▲) and green squares (■) represent the deviation of the performance in the activation loss, ohmic loss and the mass transport limited regions, respectively.

Vishvak KANNAN

Shengliang ZHANG (PhD student, NUS) is interested in dual-band electrochromic smart windows with independent control of near-infrared and visible light transmittance. His most recent work was focused on addressing the technical challenges of a new variant of electrochromic energy storage (EES) windows where an electrochromic cathode is paired with an Al anode. The EES window as-assembled is in the charge state and is recharged chemically. The Al anode-based EES windows are, however, challenged by a number of application issues such as the irreversibility of the Al anode reaction, the inconvenience of chemical

may be attributed to the strong exponential relationship between the current and the operating cell potential. Furthermore, the linear pattern of the deviations in the activation loss region and the ohmic loss region suggests that the performance is strongly correlated to the operating cell potential. The sensitivity ranks of the different stochastic parameters were calculated using a sigma-normalised derivative method along with multiple linear regression.

Vishvak reports that the calculation of the sensitivity ranks will lead to the formulation of a reduced multiple linear regression model. The advantage of deriving a reduced multiple linear regression model is that the performance of the ECR for any random set of parameters can be estimated by solving a simple linear equation instead of solving the entire mathematical model. This can be beneficial in identifying optimal operating conditions and design, live diagnosis and failure modes of the galvanic ECR.



recharging and a short cycle life. Shengliang circumvented these technical issues by modifying the Al anode with surface pre-lithiation, and demonstrated the viability of this strategy with the design of a new, electrically rechargeable dual-band electrochromic energy storage (DBEES) window. The DBEES window assembled from a pre-lithiated Al anode and a WO_{3-x} cathode delivered effective independent control of visible light and near-infrared transmittance with an impressive electrochromic performance, as well as a considerable energy storage capability.

Update on work package 2.3

Micro-variable pressure and temperature electrosynthesis plant

During this reporting period, work on the micro-variable pressure and temperature electrosynthesis plant has begun with the fabrication of two test cells and the flow loop design for electrochemical conversion and sensing systems. A key focus of the work has been on the development of robust electrode interfaces.

In the case of low temperature electrode applications, the working electrode is typically sealed in a polymeric material with an epoxy binder to provide integrity between the polymer housing and conductive substrate. However, as the temperature of the system is raised, only a select few polymer housings can be used due to the glass transition temperature (T_g) of the material. In addition the epoxy binding material is limited, which means electrode sealing and structural integrity limits the operational temperature of the electrode sensor. The testing of a diamond/boron doped diamond (BDD) electrode system is underway to assess robustness and to aid as a benchmark for less exotic electrode structures.

In previous work, BDD has been grown with diamond to produce a diamond-sealed boron doped diamond working electrode with such architectures being incorporated into ultrasonic horns, as a means of active surface cleaning of the electrode

substrate. A fully operational sensing electrode has been developed as a candidate strategy for monitoring product generation within the micro-variable pressure and temperature electrosynthesis plant. Figure 2.10 details a schematic of a current design under development in the Cambridge laboratories.

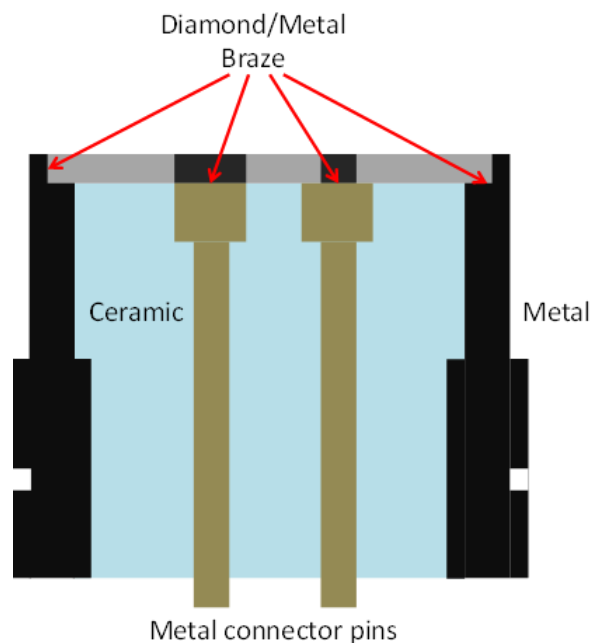


Fig. 2.10: Schematic of a current design under development in the Cambridge laboratories.

Scientific output

The following are the CREATE-acknowledged publications generated by IRP2 during the reporting period, excluding those already featured in the Scientific Highlights section on page 13.

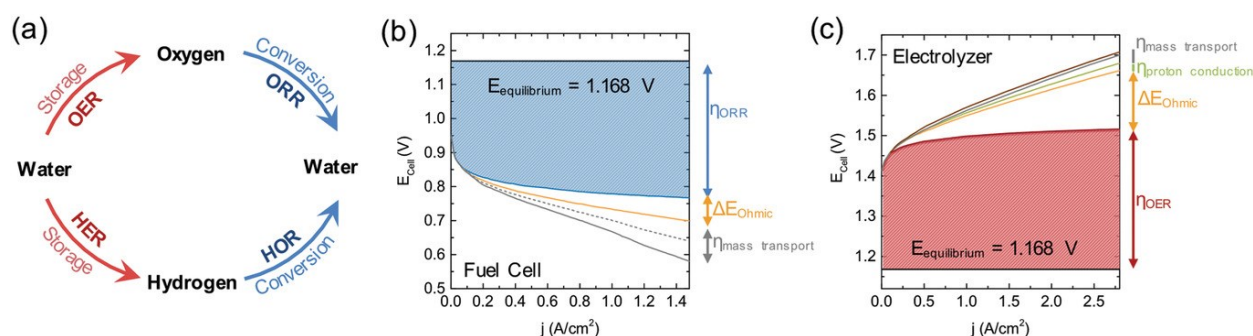
Recommended practices and benchmark activity for hydrogen and oxygen electrocatalysis in water splitting and fuel cells

Chao Wei, Reshma Rao, Jiayu Peng, Botao Huang, Ifan Stephens, Marcel Risch, Zhichuan J. Xu and Yang Shao-Horn, *Advanced Materials*

DOI: 10.1002/adma.201806296

Abstract: Electrochemical energy storage by making H₂ an energy carrier from water splitting relies on four elementary reactions, i.e., the hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR). Herein, the central objective is to recommend systematic protocols for activity measurements of these four reactions and benchmark activities for comparison, which is critical to facilitate the research and development of catalysts with high activity and stability. Details for the electrochemi-

cal cell setup, measurements, and data analysis used to quantify the kinetics of the HER, HOR, OER, and ORR in acidic and basic solutions are provided, and examples of state-of-the-art specific and mass activity of catalysts to date are given. First, the experimental setup is discussed to provide common guidelines for these reactions, including the cell design, reference electrode selection, counter electrode concerns, and working electrode preparation. Second, experimental protocols, including data collection and processing such as ohmic- and background-correction and catalyst surface area estimation, and practice for testing and comparing different classes of catalysts are recommended. Lastly, the specific and mass activity activities of some state-of-the-art catalysts are benchmarked to facilitate the comparison of catalyst activity for these four reactions across different laboratories.



A vitamin-based voltammetric pH sensor that functions in buffered and unbuffered media

Guo Xiong Tham, Adrian C. Fisher and Richard Webster, *Sensors and Actuators B: Chemical*

DOI: 10.1016/j.snb.2018.12.036

Abstract: The determination of pH using the conventional potentiometric glass electrode is widely practised in various fields ranging from academic to industrial environments. Recent research has focused on using various redox active organic and inorganic compounds as a basis of developing novel and miniaturized voltammetric pH sensors. This report describes the electrochemistry of such a sensor that is aimed to be disposable and

based on a glassy carbon (GC) electrode drop cast with redox active vitamins. Voltammetric studies in deoxygenated buffered media revealed riboflavin (VB₂) and a vitamin E derivative (VEa) to be suitable as pH-dependent and independent electroactive compounds, respectively. Solid-state square-wave voltammograms of VB₂ and VEa that were concurrently drop cast on a GC electrode in various pH deoxygenated and oxygenated buffered media yielded Nernstian responses of -54.3 and -53.4 mV/ Δ pH respectively, with the linear plot of the potential difference of VB₂ against VEa as a function of pH. Poor Nernstian responses were obtained in deoxygenated and

oxygenated non-buffered media when the pH was above approximately 4. However, with the addition of a very low concentration of an acidic buffer into the reference solution, Nernstian responses of -50.0 and -50.9 mV/ Δ pH were successfully achieved in deoxygenated and oxygen-

ated weakly-buffered media, respectively. Furthermore, a strong correlation of voltammetric versus potentiometric pH highlights the suitability of the redox active vitamin compounds as a basis for a miniaturised voltammetric pH sensor.

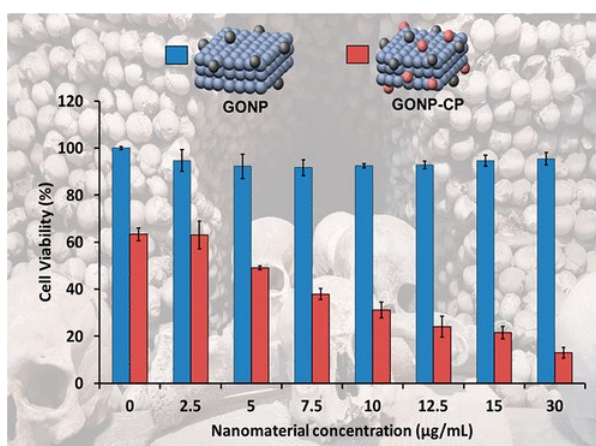
Graphene oxide nanoplatelets potentiate anticancer effect of cisplatin in human lung cancer cells

Nur Farhanah Rosli, Michaela Fojtů, Adrian C. Fisher and Martin Pumera, *Langmuir*

DOI: 10.1021/acs.langmuir.8b03086

Abstract: Graphene oxide (GO) has been widely explored by many in drug delivery strategies and toxicity assays. The toxicity of graphene oxide depends on the size of the sheets. Smaller sheets show lower toxicity, a quality which is essential for utilisation in biomedical applications. However, despite vast research on GO, anticancer properties and drug carrier capabilities of graphene oxide nanoplatelets have yet to be fully explored. Herein, we have uniquely prepared graphene oxide nanoplatelets (GONPs) from well-defined stacked graphite nanofibers (SGNF) with a base of 50×50 nm² for toxicity and drug potentiation

studies when coadministered with the chemotherapeutic drug cisplatin (CP) in human lung cancer cells, A549 cells. Results obtained from our studies have found that not only were GONPs able to act as drug carriers, but they can also significantly potentiate anticancer effect of CP in A549 cells.



Heterostructured electrocatalysts for hydrogen evolution reaction under alkaline conditions

Jumeng Wei, Min Zhou, Anchun Long, Yanming Xue, Hanbin Liao, Chao Wei and Zhichuan J. Xu, *Nano-Micro Letters*

DOI: 10.1007/s40820-018-0229-x

Abstract: The hydrogen evolution reaction (HER) is a half-cell reaction in water electrolysis for producing hydrogen gas. In industrial water electrolysis, the HER is often conducted in alkaline media to achieve higher stability of the electrode materials. However, the kinetics of the HER in alkaline medium is slow relative to that in acid because of the low concentration of protons in the former. Under the latter conditions, the entire HER process will require additional effort to obtain protons by water dissociation near or on the catalyst surface. Heterostructured catalysts, with fascinating synergistic effects derived from their heterogeneous interfaces, can provide multiple

functional sites for the overall reaction process. At present, the activity of the most active known heterostructured catalysts surpasses (platinum-based heterostructures) or approaches (noble-metal-free heterostructures) that of the commercial Pt/C catalyst under alkaline conditions, demonstrating an infusive potential to break through the bottlenecks. This review summarizes the most representative and recent heterostructured HER catalysts for alkaline medium. The basics and principles of the HER under alkaline conditions are first introduced, followed by a discussion of the latest advances in heterostructured catalysts with/without noble-metal-based heterostructures. Special focus is placed on approaches for enhancing the reaction rate by accelerating the Volmer step. This review aims to provide an overview of the current developments in alkaline HER catalysts, as well as the design principles for the future development of heterostructured nano- or micro-sized electrocatalysts.



IRP3

COMBUSTION FOR CLEANER FUELS AND BETTER CATALYSTS

To formulate the fuel of the future, IRP3 looks at new molecules that can be produced within the techno-economic constraints of a refinery and that have the potential to reduce pollutant emissions when added to fossil-derived fuels. This research will help to identify the best fuels (or fuel mixtures) for low-emission energy conversion, and to design and manufacture optimised cost-effective nanostructured materials for catalysis.

IRP3 Principal Investigators:



*Professor Markus KRAFT
University of Cambridge*



*Professor XU Rong
Nanyang Technological University*



*Assoc Professor YANG Wenming
National University of Singapore*



OVERVIEW

In our studies of hydrocarbon flames, correlating fuel structure with properties of soot formed in these flames remains a key focus. Of particular interest are alternative transportation fuels, and we are currently considering polyoxymethylene dimethyl ether (PODE) as an oxygenated, and hence low-sooting, potential substitute for diesel fuel. Being able to quantitatively characterise flames is critical to any such study. To this end, we have added yet another technique, thin filament pyrometry for temperature measurements, to our diagnostic toolbox.

In our computational investigations of Polycyclic Aromatic Hydrocarbons (PAHs), one of our main aims is to shed light on the mystery of how the first soot particles are formed from the gas phase in a combustion process. Recently, we have been focusing on curved PAHs, which possess significant electric dipoles, and how they interact with chemi-ions in flames. Such interactions are much stronger than those between neutral, flat PAHs and may help explain the inception process, i.e. how gas-phase molecules are held together by physical forces to form a new soot particle at flame temperatures.

In the field of functional inorganic nanostructured materials, we have continued to investigate amongst others flame-synthesised titanium dioxide (TiO_2) nanoparticles, both experimentally and computationally. We have further refined the ability of our detailed particle model to describe the complex morphology of aggregates, in particular with respect to sintering, and have confirmed this with experimental measurements. We have also studied experimentally the photocatalytic activity of TiO_2 , in order to decompose toxic volatile organic compounds driven by visible light for air-purification applications. As we have previously observed in our experiments that crystallinity strongly affects a number of material properties including photocatalytic performance, we are in the process of including this into our detailed particle model.

Professor Markus Kraft, PI
University of Cambridge

Update on work package 3.1

Refinery, fuel and engine of the future — experimental

Properties of surrogate fuels, marine engine after-treatment

The experimental efforts at the Department of Chemical Engineering and Biotechnology (CEB), University of Cambridge, aim at advancing the understanding of soot formation processes and the synthesis of novel nanostructures for applications in electrochemistry or photocatalysis.

In the reporting period, the work of **Dr Jochen DREYER (Research Fellow, CAM)** focused on characterising the new modular burner system

developed in Phase 1 and advancing experimental techniques to analyse the obtained flames. Some examples are Bunsen flames to determine laminar flame speeds by measuring the flame cone angle (Figure 3.1a), a range of stagnation plate stabilised flat flames for the synthesis of metal oxide nanoparticles (Figure 3.1b), and thin filament pyrometry to measure flame temperatures (Figure 3.1c).

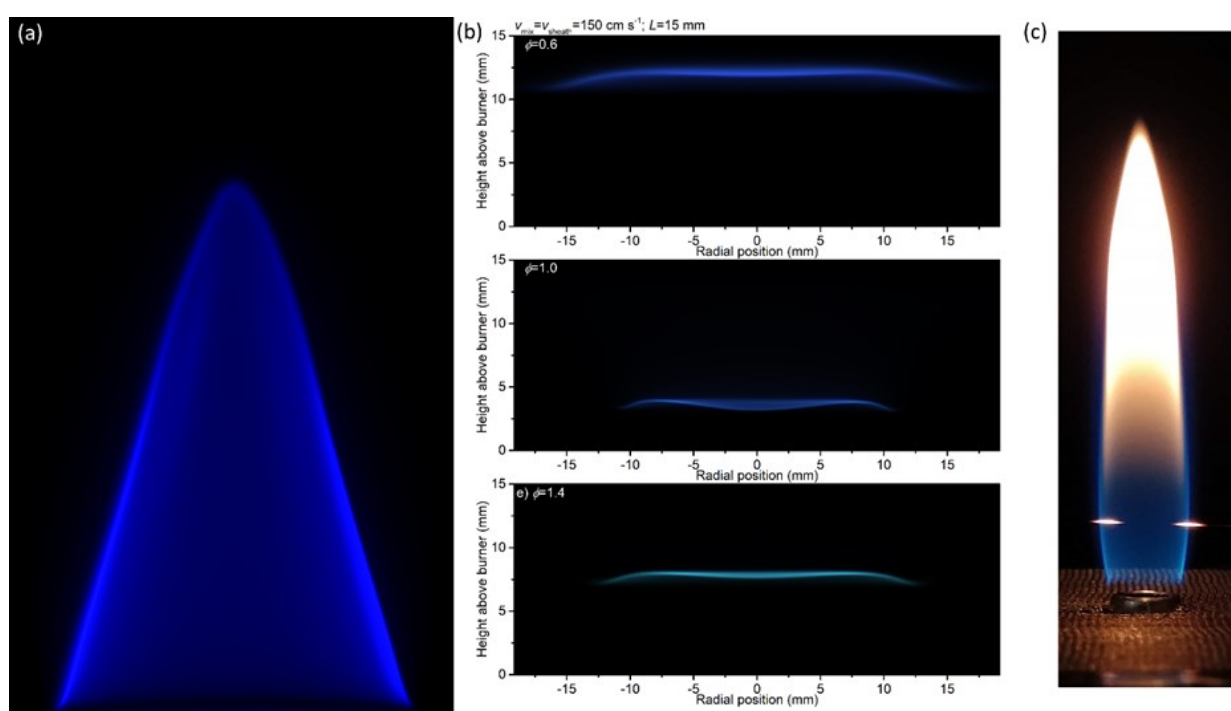


Fig 3.1: **a** Ethylene-air Bunsen flame photographed with a 430 nm band pass filter for imaging CH^* chemiluminescence. **b** Stagnation plate stabilised ethylene-air flat flames with varying equivalence ratio. **c** SiC filament inside a co-flow diffusion flame fed with pre-vaporised heptane.

Dr Jochen DREYER

Dr Maurin SALAMANCA's (Research Fellow, CAM) main research interest lies in the study of the soot formation process and the effect of biofuels on reducing pollutant formation. She has carried out a series of experiments to study the correlation between the fuel structure of cycloalkanes and cycloalkenes and the nanostructure of the soot produced in an *n*-heptane laminar co-flow diffusion flame.

The soot volume fraction (Figure 3.2) was deter-

mined by using colour ratio pyrometry with a new method for Abel transform. The addition of the cyclic fuels promotes the formation of soot in the co-flow flames. The different fuels produced benzene, a key intermediate in the soot formation process, through different routes (Figure 3.3). The fuels with double bonds (cyclohexene and cyclopentene) increase, in a higher proportion, the amount of soot produced. The main formation pathway of benzene is dehydrogenation of the

ring, besides cyclopentene can produce benzene through the fulvene pathway. Samples collected in the different flames were analysed by Raman spectrometry. The results suggest a highly disordered structure at low height above the burner.

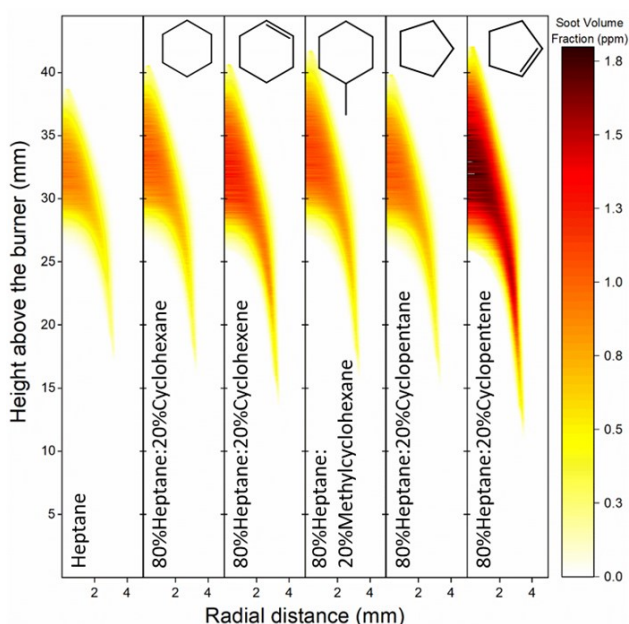


Fig 3.2: Soot volume fraction (F_v) for co-flow diffusion flames for *n*-heptane, *n*-heptane/cyclohexane, *n*-heptane/cyclohexene, *n*-heptane/methylcyclohexane, *n*-heptane/cyclopentane, and *n*-heptane/cyclopentene.

Dr Yichen ZONG (Research Fellow, NUS) has been developing cutting-edge techniques for the measurement of ultrafine particles (<100 nm) in both the combustion process and the ambient environment. He recently conducted a measurement of engine emissions in collaboration with other NUS researchers. Five different fuel mixtures have been tested under more than 100 engine conditions, with the Differential Mobility Sizer (DMS) also used in the measurement. The oxygenated fuel PODE_n has proved to be a promising alternative fuel for diesel engines. Besides this, chemiluminescence studies have been carried out on the stagnation flame for material synthesis. Both OH and CH radicals are detected for the investigation of precursor and flame chemistry during the synthesis process. Last but not least, the environmental monitoring on particulate matter (PM) emissions in the atmosphere is underway in collaboration with the researchers from National Environmental Research Institute (NERI).

Currently, a premixed burner is installed in Cambridge. This will allow study of the reduction of soot emissions with different biofuels, as well as the different physicochemical characteristics of the particles formed in premixed flames.

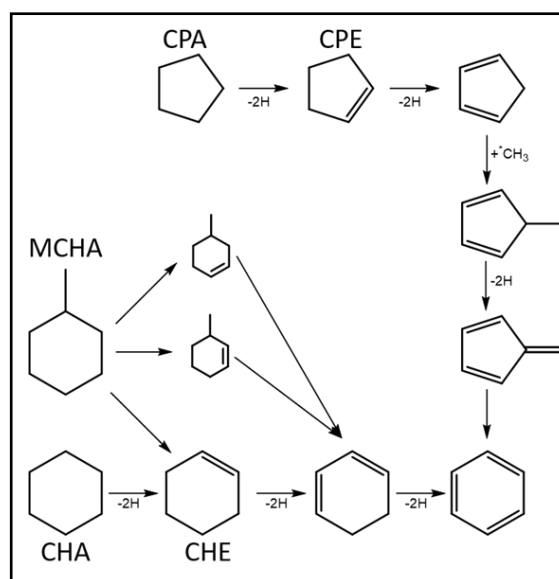


Fig 3.3: Scheme representing benzene, a key intermediate in the soot emissions, formed from the studied cyclic fuels.

Dr Maurin SALAMANCA



Fig 3.4: Diesel engine emission measurement by DMS.

Dr Yichen ZONG

TAN Yong Ren (PhD student, CAM) has just started his PhD. He is advancing in his study on the effect of PODE (polyoxymethylene dimethyl ethers) biofuel on the sooting behaviour of fuels. The PODE fuel has shown excellent soot reduction properties from Yong Ren's previous research while Project Officer at CARES, and he will be conducting in-depth study on the fuel's combustion properties. For the past few months, he has been working to assemble a premixed burner system (Figure 3.5) in order to further his PODE biofuel study, specifically to measure the particle size distribution of carbonaceous nanoparticles from the ethylene flames blended with PODE. Other than that, the formation and emission of ultrafine particles from the PODE fuel combustion will also be investigated as they have unknown geno-toxicity and are unable to be removed by a Diesel Particulate Filter (DPF) nor are they regulated in EURO 6 regulations.

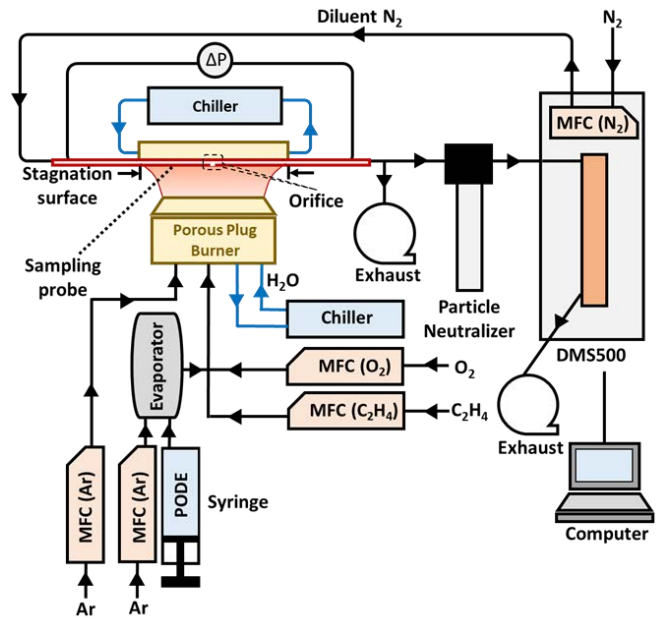


Fig 3.5: Experimental setup for the premixed burner system for PODE fuel combustion study.

TAN Yong Ren



Fig 3.6: Culture of *M. maripaludis* S2 grows to a high population using CO₂ as the only carbon source.

Clifford VO Chi Hung

Clifford VO Chi Hung's (PhD student, NUS) main research interest lies in the biological fixation of CO₂ using the archaeon *M. maripaludis* S2. Unlike many other microbes which require organic feedstock, this microorganism can convert CO₂ into CH₄ without any organic carbon input. For the past six months, Chi Hung has cultivated this archaeon in different growth environments and studied the kinetics of carbon fixation. Results revealed higher carbon fixation rate accompanied by slower death rate. The new growth environment also reduces the cost of cultivation. A publication of these results is in progress.

Update on work package 3.2

Refinery, fuel and engine of the future — modelling

Chemical mechanisms, PAH chemistry, after-treatment

Jacob MARTIN (PhD student, CAM) has been extending his investigations on the formation and thermal annealing of soot at the molecular scale. For soot formation he has been exploring the impact of aromatic molecules curved by pentagon integration into the graphene network. These strained carbon nets provide a flexoelectric permanent dipole moment, which Jacob suggests will significantly impact soot formation. To extend this work, the group has developed a new forcefield that is able to capture the flexoelectric dipole moment of these molecules using atom centred point charges with added massless charges added to the top of the aromatic bowls. Using this new forcefield, Jacob and his colleagues were able to compare the clustering dynamics of corannulene, the simplest curved PAH, and coronene, a similar sized planar PAH (Figure 3.7). The group found similar clustering behaviour of coronene and corannulene without any ions present. They then added potassium ions to the simulation. No change in the clustering dynamics was found for coronene with the ions present, which highlights the minimal interactions between the ion and the planar PAH. A significantly enhanced clustering rate with ions present was found for corannulene, which highlights the sig-

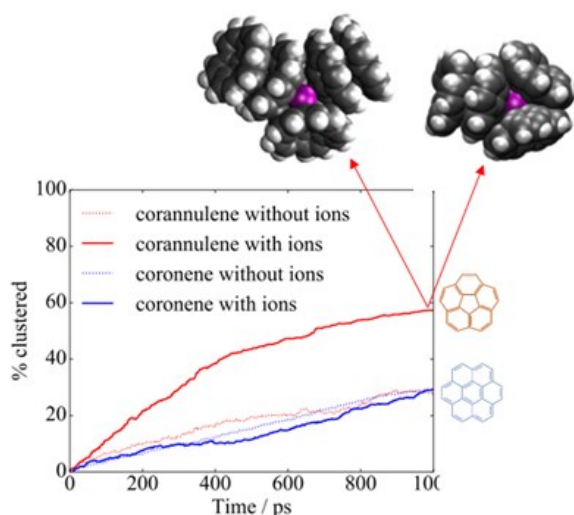


Fig 3.7: The percentage of molecules within clusters as a function of time at 500 K. Inset shows two clusters with the potassium ion in the centre coloured purple.

nificant long range interactions of ions with curved PAHs. Jacob is currently developing this forcefield to describe larger curved PAHs to study flame sized cPAHs at temperatures in the flame where soot forms.

The hardness of soot primary particles has recently been measured using nanoindentation, allowing the mechanical properties of soot to be explored. Jacob, working with a visiting student to CARES (Laura PASCAZIO), made use of reactive molecular dynamics simulations to relate the mechanical properties to the 3D connectivity within crosslinked carbon nanostructures. Figure 3.8 shows the relationship found between the crosslink density compared with the hardness. They found that for mature ethylene soot the crosslink density ranges from a polymer (CL=2 or two bonds on average per PAH) and a completely connected network (CL=3 or three bonds on average per PAH) with diesel soot having a further increase in bonding. These simulations are currently being extended to soot nanoparticles to better compare the simulations and experiments directly. If these experiments were repeated on nascent soot, it would allow relation of the mechanical properties with whether these early soot nanoparticles are liquids, polymers or 3D connected networks.

While early soot particles contain two to three crosslinks per molecule and a significant amount of hydrogen (C/H=3-5), as soot travels through the flame or a post-combustion system, carbonisation proceeds with cyclodehydrogenation producing a ring-condensed graphitic material. For soot heated to high temperatures (>3000K) it is well known that soot does not transform into graphite but to a meta-stable non-graphitising carbon material. In collaboration with the Carbon group at Curtin University, Perth, Jacob was able to develop models of these non-graphitising materials using reactive molecular dynamics simulations, which were verified against many experimental measures. Many conflicting nanostructur-

al models were reconciled in the stacked, screwed, net negative fulleroid-like nanostructure proposed (Figure 3.9). In particular, layering was found to be density driven with screw dislocations allowing the continuously curving 3D graphene nanostructure to become layered. These results provide insights into the oxidation resistance of graphitised carbon soot and potential valorisation routes for tuning this nanostructure for battery, adsorptive or catalytic applications. Jacob is aiming to present this work at the Carbon 2019 conference, and a letter has been written which is currently under review. These results apply to all non-graphitising materials such as charcoal and are an extension of the work done on the nanostructure of charcoal, which was recently published in *Environmental*

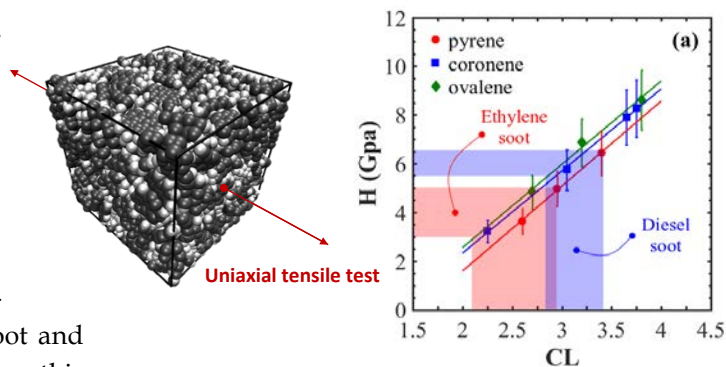


Fig 3.8: Hardness versus crosslink density relationship derived from reactive molecular dynamics simulations.

Science & Technology. Interest in charcoal for carbon sequestration has been suggested and therefore this nanostructural understanding helps to explore this possibility.

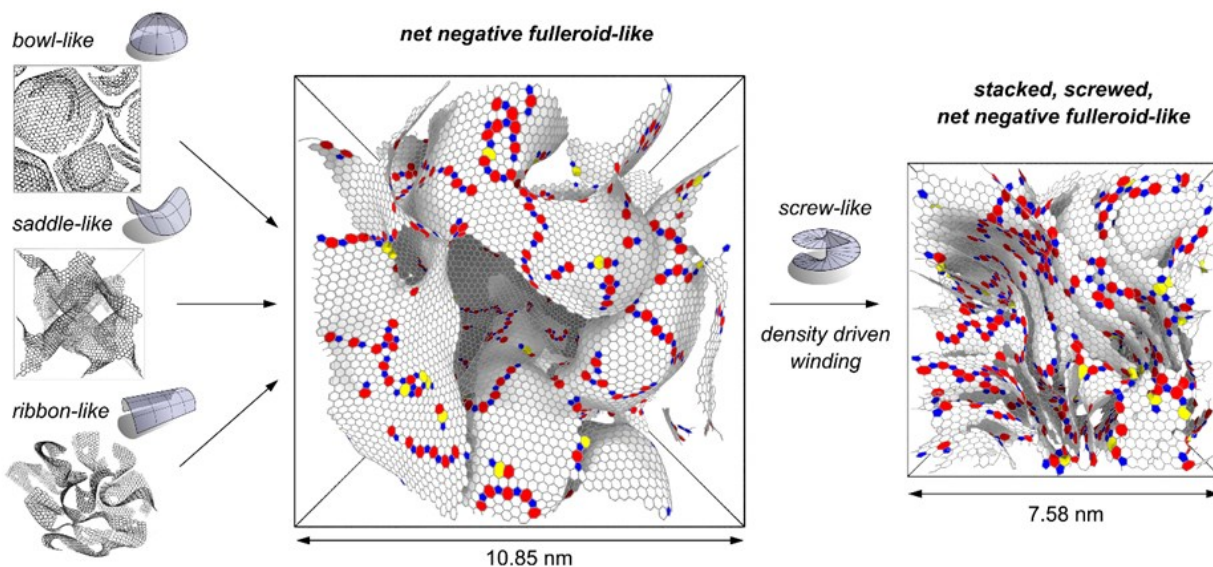


Fig. 3.9: Proposed nanostructure for low and high density isotropic carbons such as graphitised soot and carbon blacks.

Jacob MARTIN

Angiras MENON's (PhD student, CAM) work focuses on using state-of-the-art quantum chemical methods to understand the properties of polycyclic aromatic hydrocarbons (PAHs) and their role in forming soot in flames. Current calculations have focused on the optical band gap (OBG) resonantly-stabilised-radical PAHs, which have been recently suggested as new potential precursors to the formation of soot in flames. Comparison of the calculations to previous optical measurements of flames is helping to suggest what

size and shape of such radical PAHs may be relevant to soot formation. In another project completed with Jacob MARTIN (PhD student, CAM), an investigation into the stability of curved PAHs under flame conditions was conducted to further the group's work on considering curved aromatics as the precursors to soot formation. This work involved using computational chemical methods to determine both the polarity and the ability of curved aromatics to invert in flames as a function of their size and curvature. The study showed

that even moderately sized curved PAHs are unable to invert at flame temperatures, suggesting that they would possess strong polarity even at these flame conditions. The study also showed a curved PAH possessing a persistent dipole moment interacting strongly with a chemi-ion even at flame temperatures. This suggests that such interactions between curved PAHs and ions may be important. Future work will focus on understanding how curved PAHs form and interact with other species in such conditions.

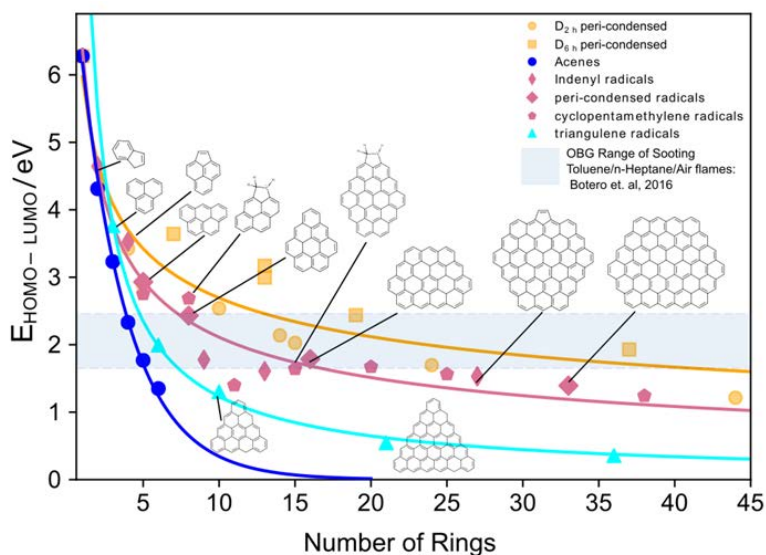


Fig 3.10: Comparison of the optical properties of resonantly stabilised radical PAHs to flat PAHs across a large size range. The radical PAHs (magenta and turquoise lines) are seen to have a lower OBG compared to their flat symmetric counterparts (yellow line).

Angiras MENON

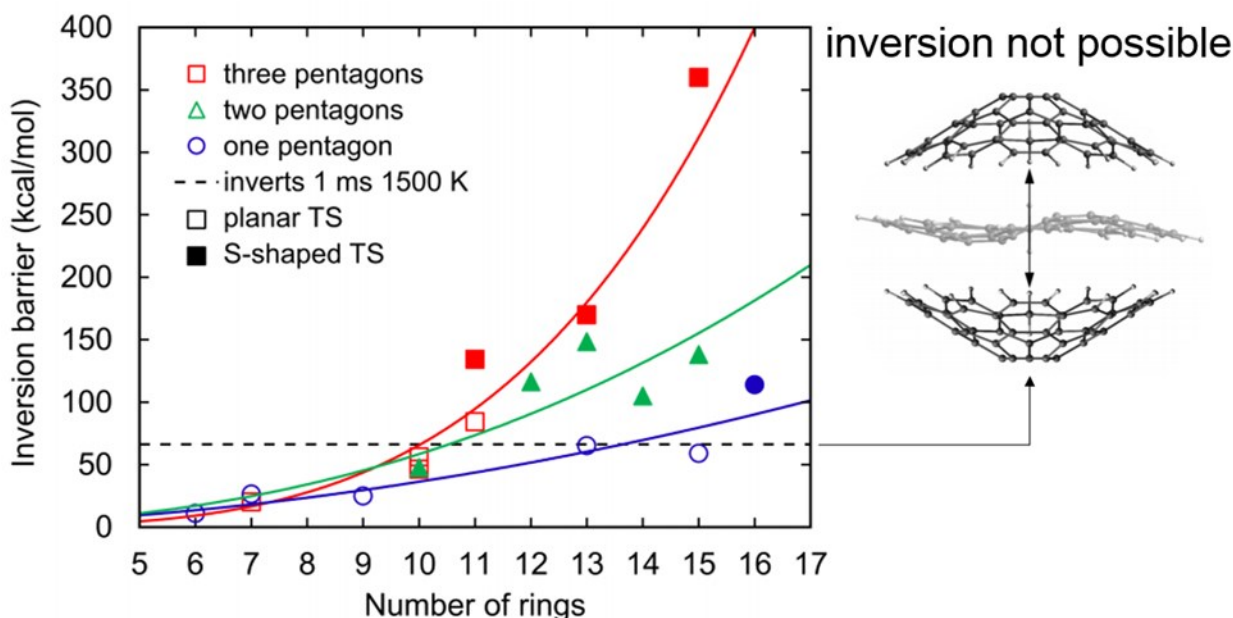


Fig. 3.11: Barrier to inversion for curved PAHs as a function of their size and shape. The dashed line highlights the threshold barrier above which inversion of curved PAHs is not expected to be possible in flames. Curved PAHs above a moderate size of 13 rings cannot invert at flame temperatures.

Angiras MENON

Image credit: Jacob MARTIN

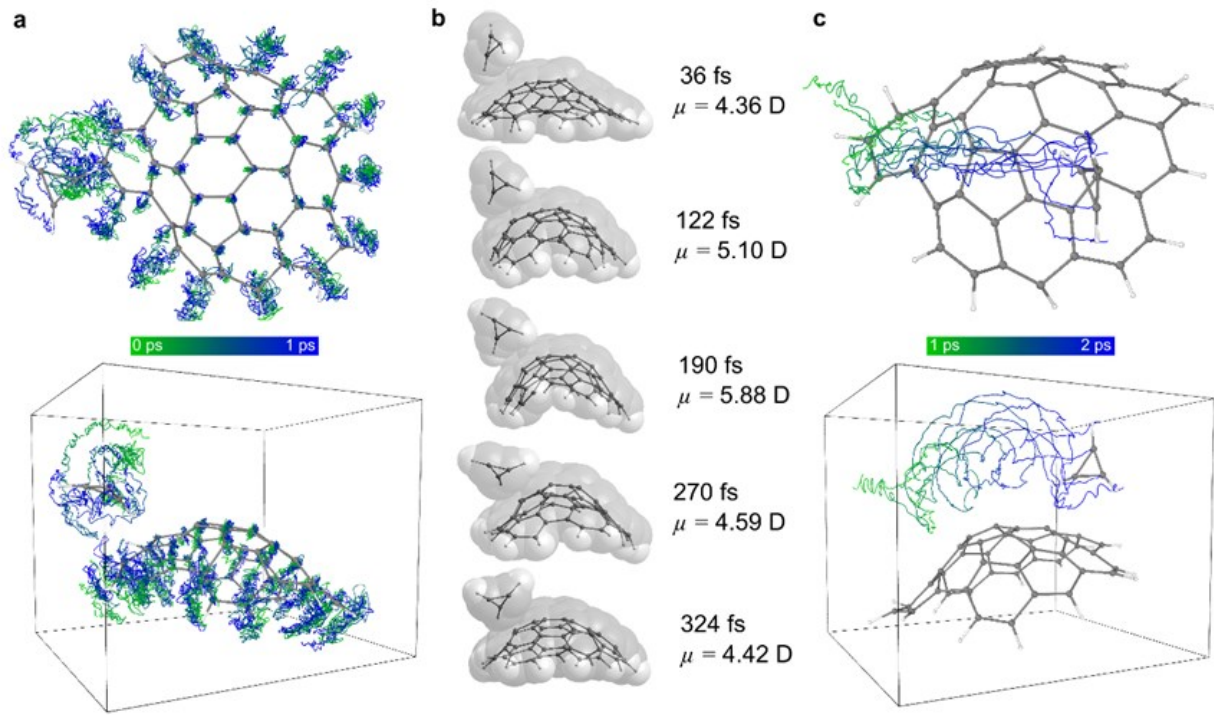


Fig. 3.12: Dynamics of a curved PAH with a chemi-ion at 1500 K, a typical flame temperature. The chemi-ion moves along the surface of the curved PAH, but the interaction remains significant across the timescale here. The dipole moment of the curved PAH remains substantial during the interaction as well.

Angiras MENON

Image credit: Jacob MARTIN

Update on work package 3.3

Better, cheaper, cleaner nanostructures — experimental

Flame synthesis of thin films of mixed metal oxide nanoparticles

On the basis of flame synthesis methods developed near the end of Phase 1, **Dr SHENG Yuan (Research Fellow, NTU)** has optimised nickel-iron-carbon nanocomposite catalysts for water splitting. The catalysts were synthesised and coated on carbon paper in one step under a pre-mixed stagnation flame to be tested without further treatment. By tuning flame equivalence ratio and concentrations of nickel/iron precursors as well as phosphorous-containing dopant introduced to the flame, the oxygen evolution overpotential at the current density of 10 mA/cm² in 1 M KOH has been reduced to 246 mV from the lowest value of 280 mV achieved in the last reporting period. Emphasis has been shifted to water splitting performance in industrially relevant high-current conditions. Encouraging preliminary results of 310 mV oxygen evolution overpotential at 300 mA/cm² have been obtained.

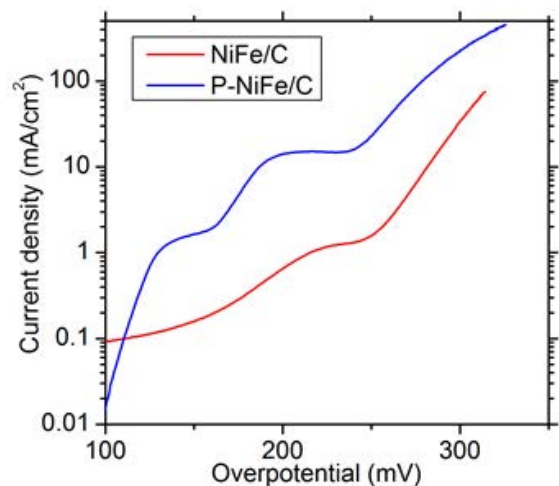
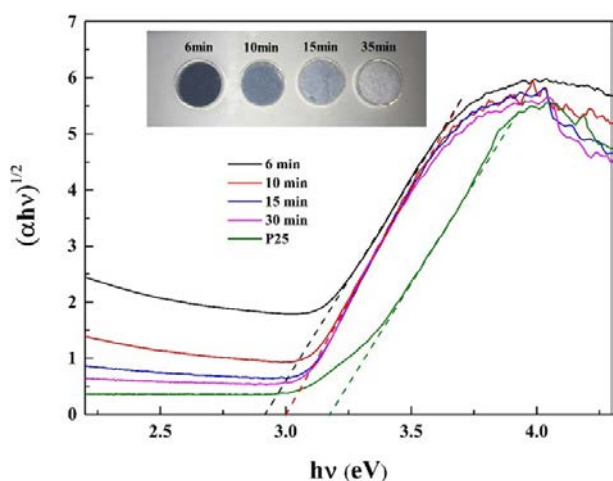


Fig. 3.13: Oxygen evolution performance (linear sweep voltammogram) of flame synthesised nickel-iron-carbon composite catalysts in 1 M KOH. NiFe/C: without phosphorous doping, P-NiFe/C: with optimal phosphorous doping.

Dr SHENG Yuan

Together with Dr Jochen DREYER (Research Fellow, CAM) and Manoel MANUPUTTY (PhD student, CAM), Dr Sheng refined the design of new modular burners for materials synthesis. He has designed and is assembling the control electronics for a new burner. They studied the polymorphism of TiO₂ nanoparticles during synthesis in premixed stagnation flames and confirmed the formation of the metastable TiO₂-II phase in such conditions for the first time, resulting in a recent publication in *Chemical Science*.

Dr Sheng and Dr LIU Guanyu (RF, eCO₂EP, NTU) have completed a comprehensive review on large-scale solar hydrogen production from water, which has been submitted to *EnergyChem*.



WU Shuyang's (PhD student, NTU) main research interest lies in the area of flame synthesised metal oxide for its application in energy and environment. His recent research has mainly focused on the investigation of the ability of blue TiO₂ on the visible-light-driven decomposition of toxic volatile organic compounds (VOCs) in order to purify the air and the study of the effect of the oxygen vacancies on the small VOCs' absorption and conversion. Through controlling the deposition time of the flame synthesis method, the quantity of defects and oxygen vacancies of TiO₂ nanoparticles can be easily tuned. Shuyang optimises the synthesis conditions to modify the bandgap of semiconductors and extend the light absorption to the visible light region. Previously, he has published a paper in *ACS Sustainable Chem. Eng* studying the photocatalytic effect of flame synthesised TiO₂ with different equivalence ratios. His aim is to seek a sustainable way to remove the various pollutants in air and water, converting them into benign and nontoxic substances.

Fig 3.14: Through controlling the quantity of defects and oxygen vacancies, the bandgap of TiO₂ can be modified in order to increase the absorption of visible light.

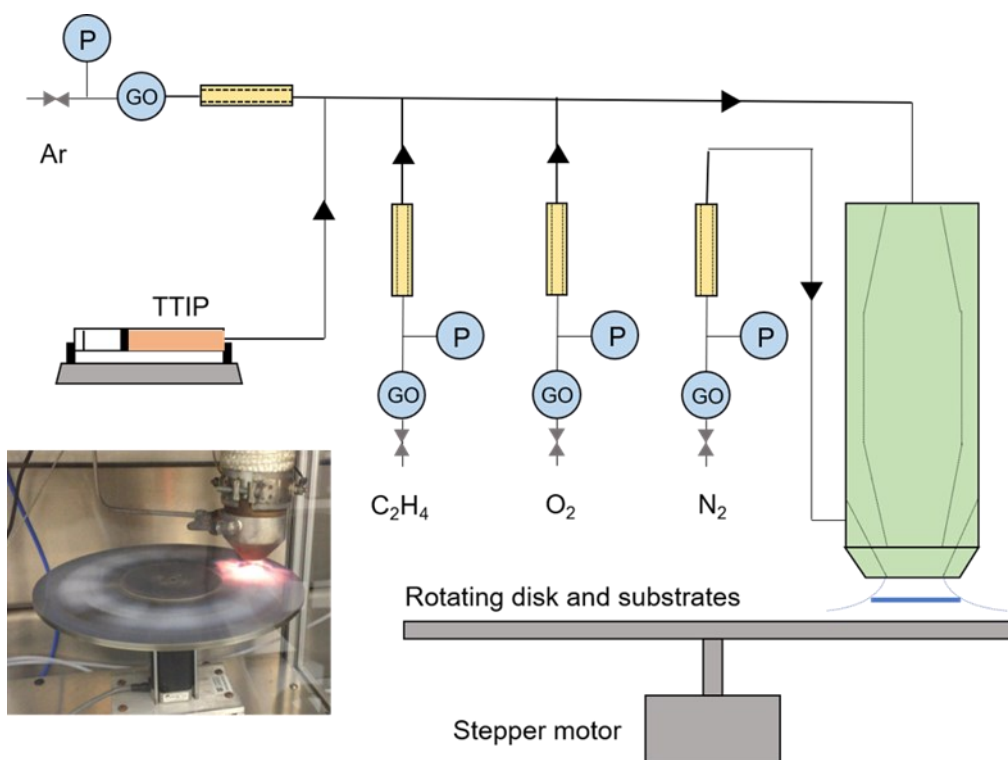


Fig 3.15: Schematic of the flame stabilised on a rotation surface (FSRS) equipment.

WU Shuyang

Update on work package 3.4

Better, cheaper, cleaner nanostructures — modelling

Gas- and surface-phase kinetics, molecular modelling and reactor optimisation

Astrid BOJE (PhD student, CAM) is working on modelling synthesis of particulate titanium dioxide (titania) using detailed population balance models. She has been studying numerical issues that arise when using population balance modelling techniques to study particle synthesis under industrial conditions, where very rapid particle formation and growth processes introduce computational challenges. She recently proposed a hybrid particle-number model and detailed particle model, implemented in the in-house population balance code (MOpS). In this new, hybrid approach, small particles are treated simply while large particles and aggregates are resolved with as much detail as possible. This allows more efficient resolution of the particle size distributions under high rate conditions and Astrid hopes to use the new approach to aid her studies of the industrial process in subsequent work.

Casper LINDBERG's (PhD student, CAM) research is focused on investigating the flame synthesis of titanium dioxide nanoparticles using detailed population balance models. He recently submitted a paper on a detailed particle model that is able to describe the complex morphology

of flame synthesised aggregate nanoparticles. Jointly with Manoel MANUPUTTY (PhD student, CAM), he used the model to simulate titanium dioxide particles formed in a stagnation flame. The study evaluated the performance of the new model against experimental data from the CARES lab, and investigated the sensitivity of key model parameters. This work is currently being prepared for publication.

Manoel MANUPUTTY (PhD student, CAM) has been working with Casper LINDBERG to perform numerical simulations of the TiO_2 -producing flames and evaluate the model predictions against his recent morphological measurements using DMS and TEM image analysis (submitted to *J. Aerosol Sci.*). The comparison (in preprint stage) has led to further understanding and improvements of model parameters, especially on particle sintering. The next step is to extend the detailed particle model to capture the nanoparticle crystallinity as it strongly affects the properties and performance of the material – as photocatalysts, for example. The model development will be guided by experimental observations which was published in his recent paper (Manuputty et al., 2019) where the presence of metastable phases was identified and the formation mechanisms of different crystalline phases in the synthesis conditions was proposed. In contrast to other proposed mechanisms in the literature, the observations suggest the importance of sub-oxide intermediates in the TiO_2 nanoparticle growth. In order to further understand the mechanism of the early stage TiO_2 nanoparticles in flame, Manoel is also working with Dr Yichen ZONG to set up an *in situ* diagnostic technique using Raman scattering.

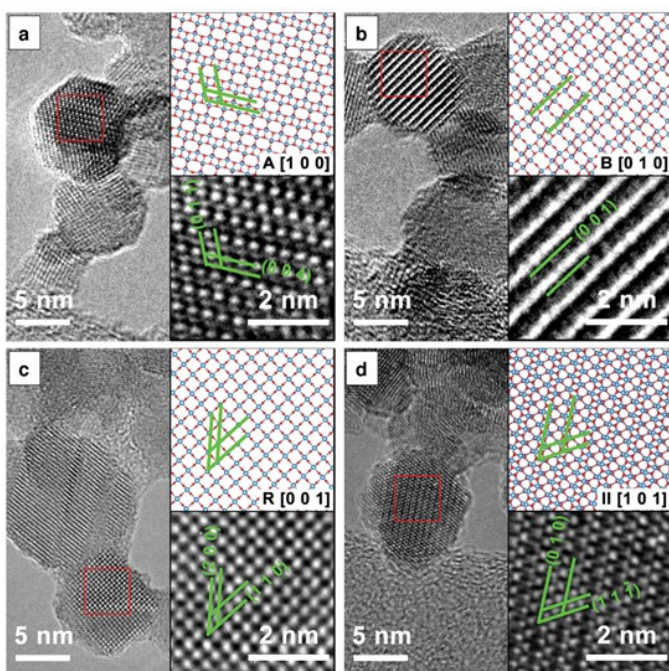


Fig 3.16: High-resolution TEM images of the four TiO_2 crystalline phases identified at different flame equivalence ratios showing the crystal lattices accompanied by the corresponding ball-and-stick models.

Manoel MANUPUTTY

Scientific output

The following are the CREATE-acknowledged publications generated by IRP3 during the reporting period, excluding those already featured in the Scientific Highlights section on page 13.

Ion-induced soot nucleation using a new potential for curved aromatics

Kimberly Bowal, Jacob W. Martin, Alston J. Misquitta and Markus Kraft, *Combustion Science and Technology*

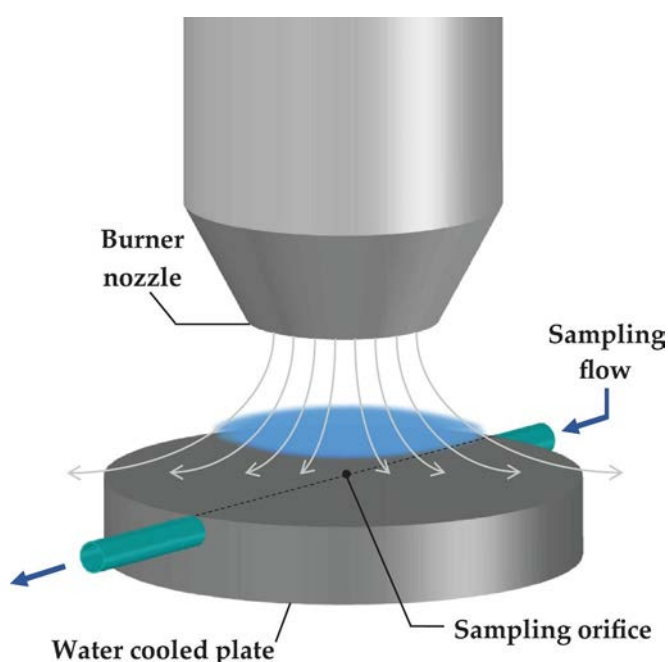
DOI: 10.1080/00102202.2019.1565496

Abstract: A potential able to capture the properties and interactions of curved polycyclic aromatic hydrocarbons (cPAHs) was developed and used to investigate the nucleation behavior and structure of nascent soot particles. The flexoelectric charge polarization of cPAHs caused by pentagon integration was included through the introduction of off-site virtual atoms, and enhanced dispersion interaction parameters were fitted. The electric polarisation and intermolecular interactions of cPAHs were accurately reproduced compared to *ab initio* calculations. This potential was used within molecular dynamics simulations to examine the homogeneous and heterogeneous nucleation behavior of the cPAH corannulene

and planar PAH coronene across a range of temperatures relevant to combustion. The enhanced interactions between cPAHs and potassium ions resulted in significant and rapid nucleation of stable clusters compared to all other systems, highlighting their importance in soot nucleation. In addition, the resulting cPAH clusters present morphologies distinct from the stacked planar PAH clusters.



A two-step simulation methodology for modelling stagnation flame synthesised aggregate nanoparticles



Casper S. Lindberg, Manoel Y. Manuputty, Jethro Akroyd and Markus Kraft, *Combustion and Flame*

DOI: 10.1016/j.combustflame.2019.01.010

Abstract: A two-step simulation methodology is presented that allows a detailed particle model to be used to resolve the complex morphology of aggregate nanoparticles synthesised in a stagnation flame. In the first step, a detailed chemical mechanism is coupled to a one-dimensional stagnation flow model and spherical particle model solved using method of moments with interpolative closure. The resulting gas-phase profile is post-processed with a detailed stochastic population balance model to simulate the evolution of the population of particles, including the evolution of each individual primary particle and their connectivity with other primaries in an aggregate.

A thermophoretic correction is introduced to the post-processing step through a simulation volume scaling term to account for thermophoretic transport effects arising due to the steep temperature gradient near the stagnation surface. The methodology is evaluated by applying it to a test case: the synthesis of titanium dioxide from titanium tetraisopropoxide (TTIP) precursor. The

thermophoretic correction is shown to improve the fidelity of the post-process to the first fully-coupled simulation, and the methodology is demonstrated to be feasible for simulating the morphology of aggregate nanoparticles formed in a stagnation flame, permitting the simulation of quantities that are directly comparable to experimental observations.

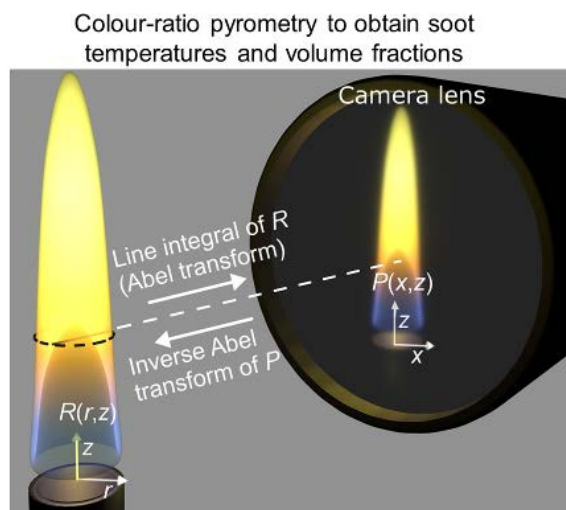
Improved methodology for performing the inverse Abel transform of flame images for color ratio pyrometry

Jochen A. H. Dreyer, Radomir I. Slavchov, Eric J. Rees, Jethro Akroyd, Maurin Salamanca, Sebastian Mosbach and Markus Kraft, *Applied Optics*

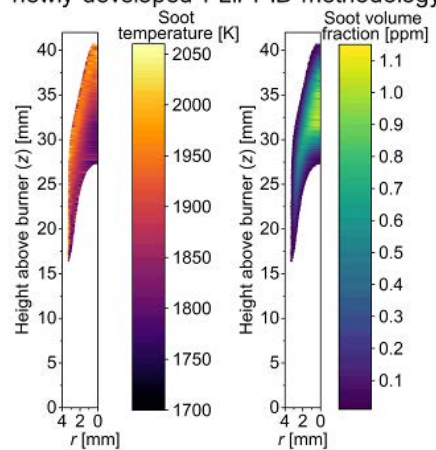
DOI: 10.1364/AO.58.002662

Abstract: A new method is presented for performing the Abel inversion by fitting the line-of-sight projection of a predefined intensity distribution (FLiPPID) to the recorded 2D projections. The aim is to develop a methodology that is less prone to experimental noise when analyzing the projection of axisymmetric objects—in this case, co-flow diffusion flame images for color ratio pyrometry. A regression model is chosen for the light emission intensity distribution of the flame cross section as a function of radial distance from the flame center line. The forward Abel transform of this model

function is fitted to the projected light intensity recorded by a color camera. For each of the three color channels, the model function requires three fitting parameters to match the radial intensity profile at each height above the burner. This results in a very smooth Abel inversion with no artifacts such as oscillations or negative values of the light source intensity, as is commonly observed for alternative Abel inversion techniques, such as the basis-set expansion or onion peeling. The advantages of the new FLiPPID method are illustrated by calculating the soot temperature and volume fraction profiles inside a co-flow diffusion flame, both being significantly smoother than those produced by the alternative inversion methods. The developed FLiPPID methodology can be applied to numerous other optical techniques for which smooth inverse Abel transforms are required.



Smoother inverse Abel transforms with newly developed FLiPPID methodology



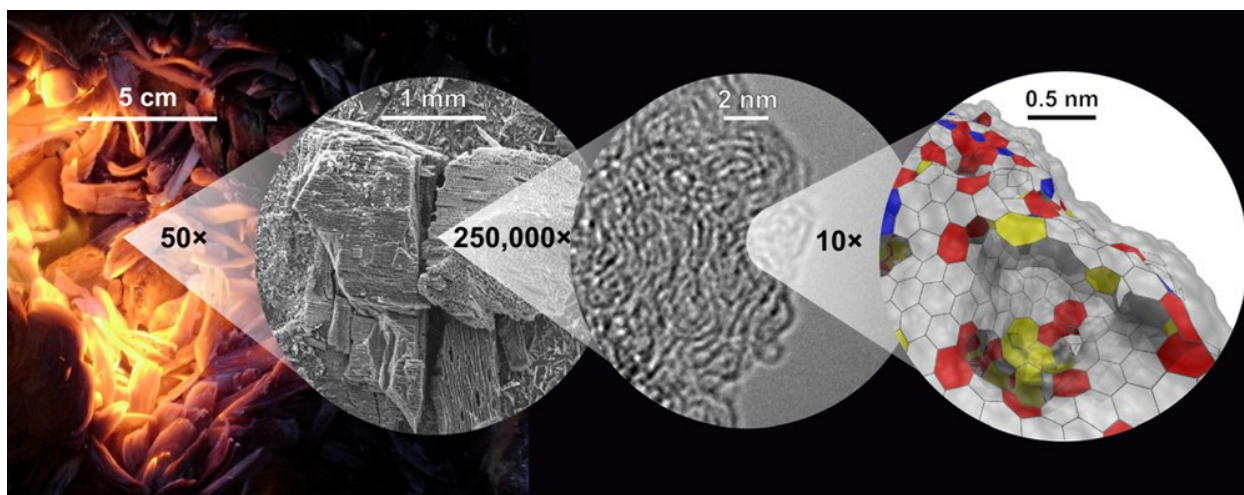
Nanostructure of gasification charcoal (biochar)

Jacob W. Martin, Leonard Nyadong, Caterina Ducati, Merylyn Manley-Harris, Alan G. Marshall and Markus Kraft, *Environmental Science & Technology*

DOI: 10.1021/acs.est.8b06861

Abstract: In this work, we investigate the molecular composition and nanostructure of gasification charcoal (biochar) by comparing it with heat-treated fullerene arc-soot. Using ultrahigh resolution Fourier transform ion-cyclotron resonance and laser desorption ionisation time-of-flight mass spectrometry, Raman spectroscopy, and high resolution transmission electron microscopy we analysed charcoal of low tar content obtained from gasification. Mass spectrometry revealed no

magic number fullerenes such as C_{60} or C_{70} in the charcoal. The positive molecular ion m/z 701, previously considered a graphitic part of the nanostructure, was found to be a breakdown product of pyrolysis and not part of the nanostructure. A higher mass distribution of ions similar to that found in thermally treated fullerene soot indicates that they share a nanostructure. Recent insights into the formation of all carbon fullerenes reveal that conditions in charcoal formation are not optimal for the formation of fullerenes, but instead, curved carbon structures coalesce into *fulleroid-like* structures. Microscopy and spectroscopy support such a *stacked, fulleroid-like* nanostructure, which was explored using reactive molecular dynamics simulations.

**Modelling soot formation in a benchmark ethylene stagnation flame with a new detailed population balance model**

Dingyu Hou, Casper S. Lindberg, Manoel Y. Manuputty, Xiaoqing You and Markus Kraft, *Combustion and Flame*

DOI: 10.1016/j.combustflame.2019.01.035

Abstract: Numerical simulation of soot formation in a laminar premixed burner-stabilised benchmark ethylene stagnation flame was performed with a new detailed population balance model employing a two-step simulation methodology. In this model, soot particles are represented as aggregates composed of overlapping primary particles, where each primary particle is composed of a number of polycyclic aromatic hydrocarbons (PAHs). Coordinates of primary particles are tracked, which enables simulation of particle

morphology and provides more quantities that are directly comparable to experimental observations. Parametric sensitivity study on the computed particle size distributions (PSDs) shows that the rate of production of pyrene and the collision efficiency have the most significant effect on the computed PSDs. Sensitivity of aggregate morphology to the sintering rate is studied by analysing the simulated primary particle size distributions (PPSDs) and transmission electron microscopy (TEM) images. The capability of the new model to predict PSDs in a premixed stagnation flame is investigated. Excellent agreement between the computed and measured PSDs is obtained for large burner-stagnation plate separation (≥ 0.7 cm) and for particles with mobility diameter larger than 6 nm, demonstrating the ability of this new model to describe the coagulation process of aggregate particles.

Bivariate extension of the moment projection method for the particle population balance dynamics

Shaohua Wu, Casper S. Lindberg, Jethro Akroyd, Wenming Yang and Markus Kraft, *Computers & Chemical Engineering*

DOI: 10.1016/j.compchemeng.2018.12.011

Abstract: This work presents a bivariate extension of the moment projection method (BVMPM) for solving the two-dimensional population balance equations involving particle inception, growth, shrinkage, coagulation and fragmentation. A two-dimensional Blumstein and Wheeler algorithm

is proposed to generate a set of weighted particles that approximate the number density function. With this algorithm, the number of the smallest particles can be directly tracked, closing the shrinkage and fragmentation moment source terms. The performance of BVMPM has been tested against the hybrid method of moments (HMOM) and the stochastic method. Results suggest that BVMPM can achieve higher accuracy than HMOM in treating shrinkage and fragmentation processes where the number of the smallest particles plays an important role.

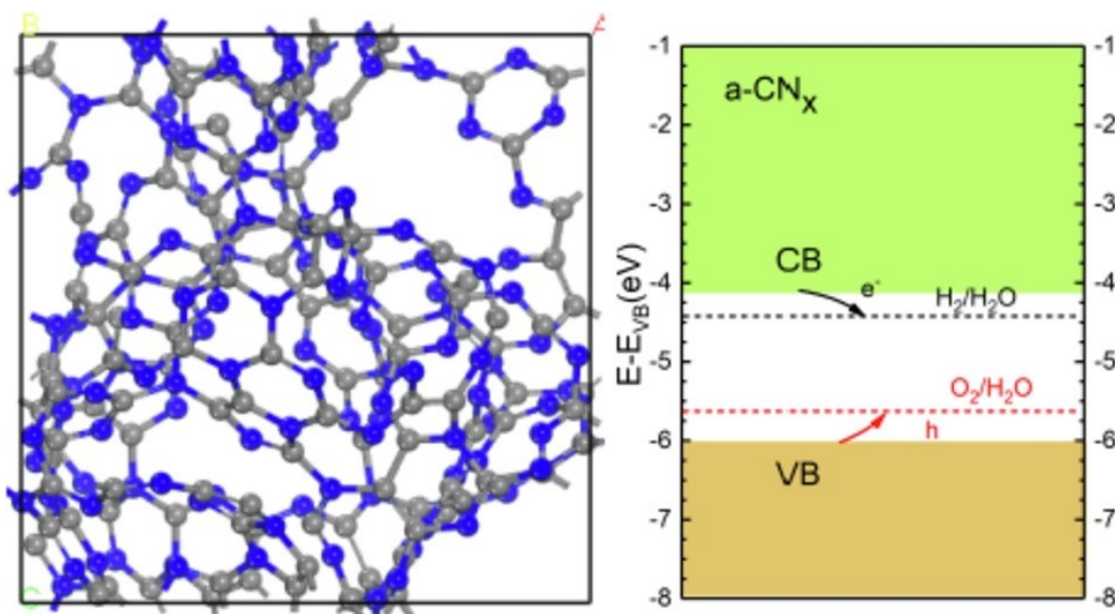
Atomic structure and electronic structure of disordered graphitic carbon nitride

Haichang Lu, Yuzheng Guo, Jacob W. Martin, Markus Kraft and John Robertson, *Carbon*

DOI: 10.1016/j.carbon.2019.03.031

Abstract: Random networks of sp^2 bonded amorphous graphitic carbon nitride (g-CN) have been created by density functional molecular dynamics calculations. A direct molecular dynamics approach was found to create a network with too many like-atom bonds so that an indirect method

via an h-BN random network is used. The resulting network possesses the local units of melems found in the crystalline g- C_3N_4 lattice. The networks have the electron affinity and ionisation potential values compatible with photocatalytic water splitting. They are found to possess too many defects so that the band gap is smaller than found experimentally.



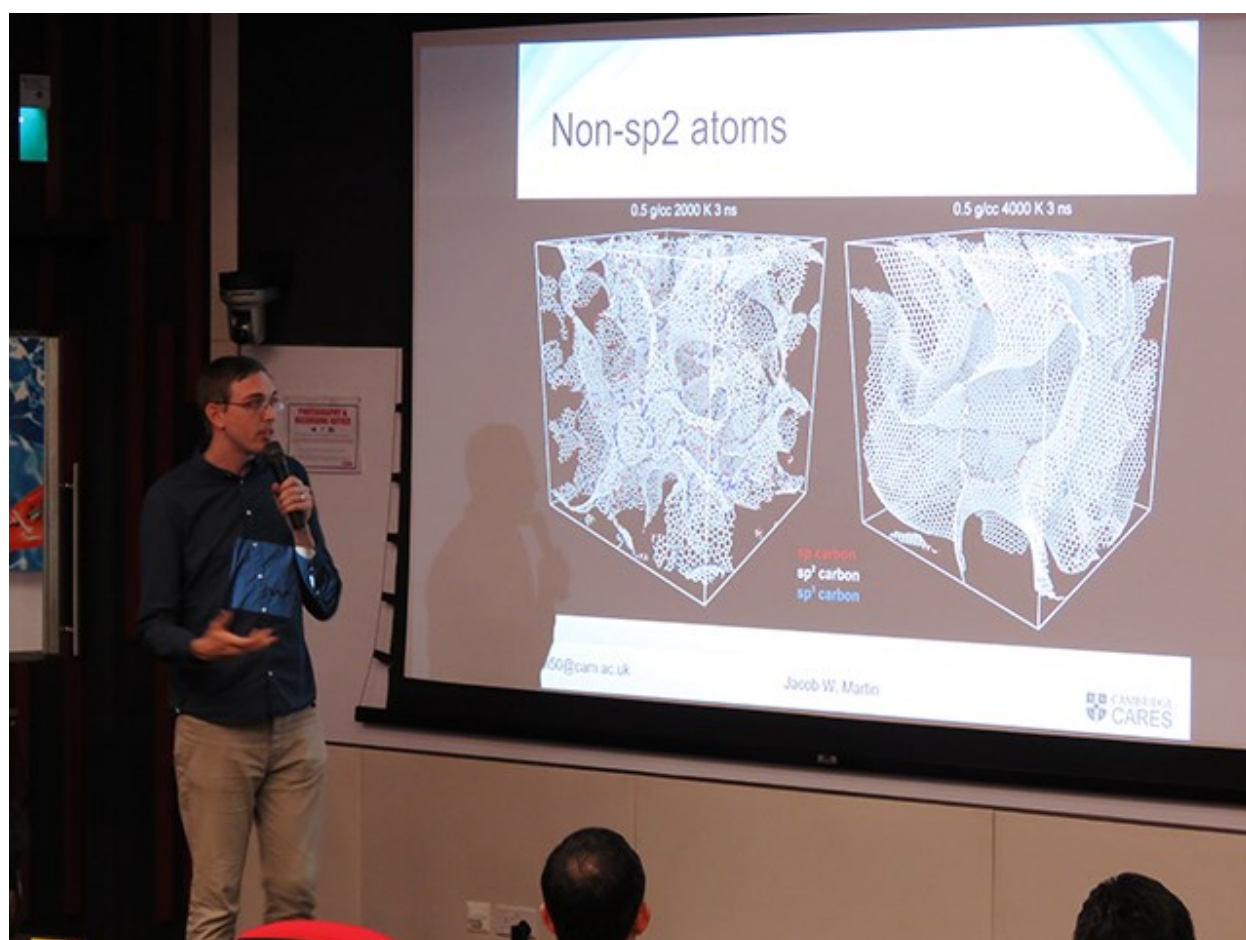
Other activities and achievements

Astrid BOJE (PhD student, CAM) presented a paper with the title 'Numerical Study of the Evolution of Particle Size and Morphology in an Industrial Titanium Dioxide Reactor' (co-authored by Jethro Akroyd and Markus Kraft) at the annual AIChE conference in Pittsburgh, USA from 28 October - 2 November 2018.

Astrid also presented work at the six-monthly meeting with her industrial sponsor Venator in November 2018.

Jacob MARTIN (PhD student, CAM) presented work on 'Adding another dimension to graphene: topology of 3D graphene networks' as a poster and talk at the 9th International Conference on Advanced Materials and Nanotechnology in Wellington, New Zealand from 10-14 February 2019.

Jacob also gave an invited talk on 'Insights into the nanostructure of biochar: ribbon-like or fullerene-like?' at the 3rd E2S2-CREATE Biochar Workshop in Singapore on 16 January 2019 (image below).





IRP4



BETTER, CLEANER HEAT USAGE

Better, Cleaner Heat Usage is a new IRP4 for Phase 2, replacing the former energy/electricity focus in Phase 1. This work is focused on high-performance thermal management and waste heat recovery research for improved, i.e. cleaner and more efficient heat usage in energy conversion technologies. IRP4 addresses two key challenges in power generation systems: a) the efficient management of heat and b) the emission of harmful pollutants, which is particularly problematic in fuel-based technologies such as diesel engine power plants or marine engines. Regulations are increasingly stringent for these systems and a full understanding of the underlying phenomena is necessary to tackle this problem.

IRP4 Principal Investigators:



*Professor Epaminondas MASTORAKOS
University of Cambridge*



*Professor Alessandro ROMAGNOLI
Nanyang Technological University*



*Professor LEE Poh Seng
National University of Singapore*



OVERVIEW

The use of fossil or biomass-derived fuels for electrical power or mechanical work generation accounts for some 85% of the global primary energy supply at present, and this percentage is not likely to drop below 50% by 2050 even in aggressive CO₂ abatement scenarios. Most of this energy comes to us through combustion in piston engines, gas turbines and burners in manufacturing processes and domestic and commercial heating applications. Burning fuels to create work involves, by thermodynamic necessity, large amounts of waste heat. The most modern combined-cycle gas turbine plant may now reach efficiencies up to 64%, while the most efficient large engines used in marine transport may go as high as 55%. This efficiency is defined as the ratio of useful mechanical output to the thermal energy contained in the fuel. Although these numbers are impressive, if one considers what they were twenty years ago, they are quite worrying if one realises that the remaining energy is actually wasted in the form of heat. Hence, anything one can do to utilise the wasted energy can have enormous financial, but also CO₂ emissions, implications. Furthermore, if one considers that the energy density of present and future batteries still has a long way to go to make them competitive to liquid fuels for marine and air transport, one concludes that the reciprocating engine and the gas turbine will be with us for a long time and hence the associated physical phenomena must be studied so as to enable further innovations.

An additional worry with fuel usage is the non-CO₂ pollutants emitted by combustion processes. Such pollutants include NO_x, soot and other particulate matter (PM), CO, unburnt hydrocarbons and SO₂. For decades now, reducing these emissions has been a driving factor for improving combustion technologies and huge advancements have already been made. These developments have been motivated by the strict legislation on the maximum amount of pollutants that are legally produced per unit of fuel burnt, and are enabled by innovative designs that arise from better physical understanding achieved through fundamental research. However, with the increase in population and the increase of fuel and energy use per capita, and the ever-increasing realisation that exposure to these pollutants has very serious adverse health effects, there is an urgent need to develop combustion technologies that emit less soot and NO_x.

In this context, this IRP examines the combustion process inside one of the most important prime movers for the world and for Singapore: the marine engine. The research team aims to develop (i) new knowledge and more accurate simulation tools for marine or other engines, including the fluid mechanics, the chemistry and the thermodynamics, which can then allow us to estimate the changes in pollutants or efficiency if one switches fuels or uses additives, such as those examined in IRP3; (ii) more efficient ways to harness the waste heat through novel turbomachinery cycles, which can increase the overall efficiency; (iii) more effective heat exchangers for capturing the sensible enthalpy of the exhaust gases, a development that can reduce weight, footprint and cost; and (iv) a simple-to-use computational framework where

energy use, CO₂ emission, NO_x and particulate emissions from shipping can be estimated to an accuracy that can inform fleet operators and port authorities who may then implement novel low-emission policies. These objectives will be addressed in interacting Work Packages, as described briefly below. The outcomes are not limited to marine engines, but can be used to a large extent throughout the spectrum of fuel technologies. The work is based on simulation tools and experiments at various labs and across the physico-chemical lengthscales, from the o(nm) particles associated with soot production to the o(m) size

of marine engine cylinders and heat exchangers.

This IRP is new in C4T and the work has just started with the recruitment procedures recently completed in March 2019. In the text below, some specific examples are given to introduce the techniques and the nature of the results to be developed.

Professor Epaminondas Mastorakos, PI
University of Cambridge

Update on work package 4.1

Engine combustion — best fuel, best operating condition

Objectives and methodology: The flow inside engines is turbulent and the chemistry of combustion and pollutant formation is highly sensitive to temperature and species mass fractions fluctuations. Hence, special theories are needed to overcome this inherent non-linearity and stochasticity. In this Work Package, the Conditional Moment Closure (CMC) and the Stochastic Reactor Model (SRM) will be applied to the case of the marine engine, with various levels of sophistication of the underlying flow and spray pattern, in order to improve the accuracy by which soot and NO_x are produced, as a function of fuel type, additive, and operating condition. Multi-dimensional Computational Fluid Dynamics (CFD) codes will be run for such cases and detailed fuel chemistry and soot emission mechanisms will be implemented. Validation will be performed by comparison with engine data (some from IRP3) and chemical and soot mechanisms from IRP3 will be implemented. The outcome will be highly-refined simulations of the

two-phase and multi-scale processes occurring inside the engine. By nature, these simulations need access to supercomputers and will be executed at the Cambridge University and Singapore Supercomputer Centres.

In addition, experimental data from IRP3 and simulation data from the CFD above across a range of engines will be used to calibrate low-order thermodynamic models that will be developed further to include soot and NO_x and not just pressure and temperature that are the usual outputs at present. This will allow such low-order models, that can be run at low-cost at the fleet engineering office level, to be able to predict pollutant emissions from a particular ship given its fuel consumption, load and rpm. This information will then be delivered to the J-Park Simulator (WP4) in order to assess the overall environmental impact of shipping for Singapore.

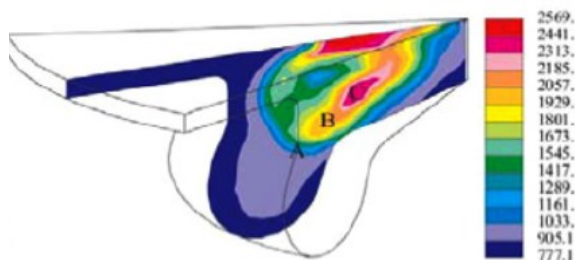


Fig 4.1: Ensemble-averaged temperature distribution in K from a small-bore diesel engine after autoignition (from Da Paola et al., *Combustion Science and Technology* 180:883-899, 2007).

Preliminary results: Figure 4.1 (previous page) shows the temperature field produced by CFD supplemented with the CMC model for a small light-duty truck diesel engine, as an example of the nature of results achievable with CFD applied

to engines. In this WP, similar simulations but with detailed fuel-specific chemistries and including PM production will be performed for the case of large marine engines with focus on predicting combustion behavior and emissions.

Update on work package 4.2

Closed power cycles — selection and analysis

Objectives and methodology: Due to 2nd Law limitations, it is not possible to turn all the energy of the fuel into work. However, current engines operate quite far from this limit and hence there is potential for improved efficiency. Further, methods that use the energy of the exhaust gases, either as heat or as work, will result in less fuel burn per unit of economic benefit. Such methods include the development of bottoming cycles using the Rankine cycle paradigm but with organic working fluids in order to match the lower evaporation temperatures associated with low-grade waste heat (“Organic Rankine Cycle” - ORC). In this Work Package, such cycles will be tested computationally and experimentally (for some specific component) under conditions appropriate for medium to large engines size. In addition, novel ways to harness the waste heat will be explored, including novel turbomachinery design such as the Multi-Injection Turbine Housing concept; such a concept offers opportunity to improve turbine by more than 2% by simply mitigating the tip-leakage loss.

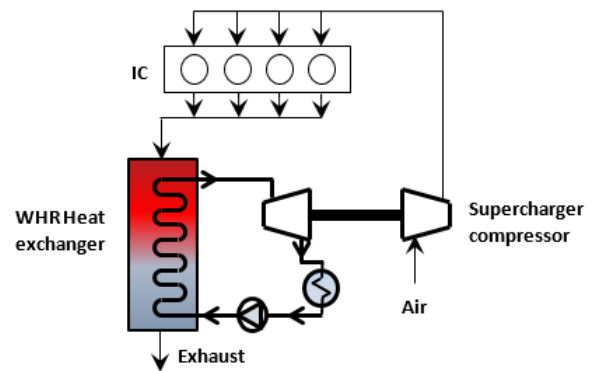


Fig 4.2: Novel concept for exhaust gas energy use in a supercharger. Note that the work to drive the compressor is now coming from the exhaust gases indirectly.

Figure 4.2 shows one of the interesting concepts that will be explored in this work. Instead of the enthalpy of the exhaust gases driving the turbo-charger directly, they instead give heat to a different working fluid that then drives the turbine.

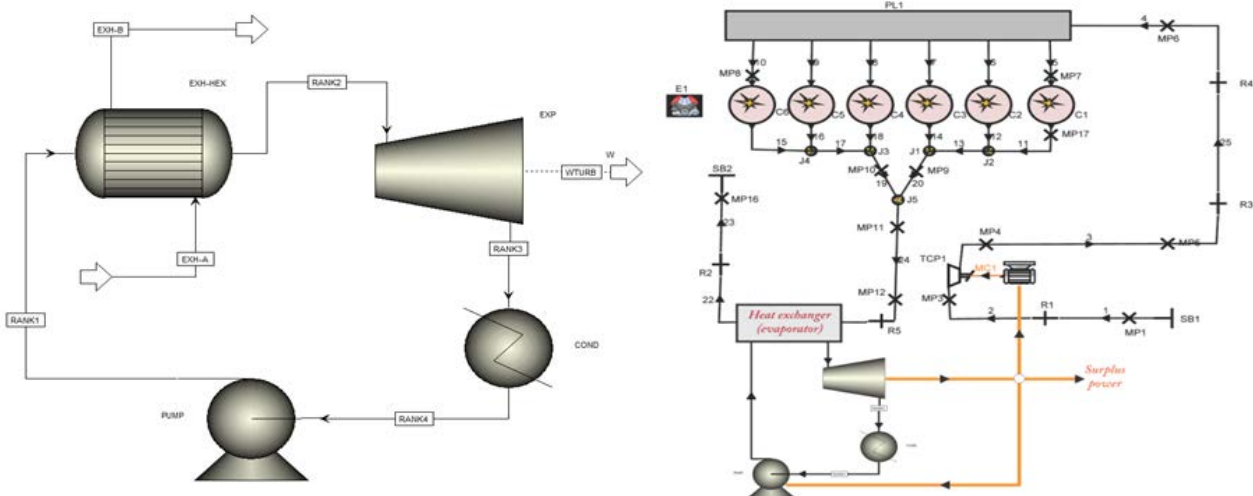


Fig 4.3: a ORC and b engine models.

This allows greater flexibility and increases engine efficiency by reducing the back pressure.

Preliminary results: Figure 4.3 shows how a Rankine cycle model and an engine model are linked together. The left figure shows a schematic diagram of the Rankine cycle process as modeled in the software Aspen Plus®. The fluid properties are calculated with the property method using the Peng-Robinson equation of state. The Rankine cycle in this study is the basic layout without any regenerator. The organic working media cycles through the four basic components in the following order. First the exhaust heat recovery heat exchanger/evaporator with a fixed exhaust outlet temperature and a minimum pinch point temperature allowed of 30 °C. Secondly the turbine expander, with a fixed outlet pressure equal to the condenser pressure and outlet enthalpy determined by the given isentropic efficiency. Third,

the condenser, at constant pressure and outlet condition assumed at saturated liquid state. Finally the pump, with an outlet pressure. This will affect only the calculation of fluid constant pressure specific heat at a prescribed value and fixed isentropic efficiency. Both the pump outlet pressure and Rankine fluid mass flow are parametric variables at design point. Figure 4.3b illustrates how the information between the engine and Rankine model needs to be linked together. For the engine model, the pressure and temperature loss at exhaust heat exchanger/evaporator has to be defined according to the Rankine cycle demand.

Update on work package 4.3

High-efficiency heat exchanger

Objectives: IRP4 is focused on high-performance thermal management and waste heat recovery research for improved and more efficient heat usage in energy conversion technologies. Its main objective is to model and optimise a full power generation system in terms of heat management and combustion emissions. The specific objectives for WP3 are:

- Development of compact heat exchangers such as micro-channel heat exchangers for use in industrial environments.
- Development of air-cooled heat exchangers that can replace water-cooled units to reduce water use and associated energy use.

Methodology:

Development of new types of compact heat exchangers

Use of new materials and fabrication techniques to manufacture heat exchangers consisting of a large number of miniature channels. The performance of a heat exchanger in terms of heat transfer is directly related to the characteristic flow diameter. The smaller the diameter, the higher the heat transfer rate, but this can also increase the energy used to move it through the channel. As such, the challenge is to maintain a good balance between heat transfer enhancement and pressure drop penalty.

Performance enhancement of plate heat exchangers and double tube heat exchangers by exploiting novel fin structures

In particular, the novel oblique fin structure will be adapted to enhance the heat transfer rate in different types of compact heat exchangers, downsize the heat exchangers and reduce the pumping power needed. Double-layered and tight contact tube walls or plates will be placed between refrigerant and water to ensure good conduction between the two working media as well as create a small air gap. By introducing such small air gap between refrigerant and water, the safety of the whole system is guaranteed as leakages can be easily detected by monitoring the pressure of the air gap. The tube walls or plates on the both sides of the air gap will be tightly contacted while maintaining such air gap.

Numerical and experimental research of the thermal performance of the proposed novel heat exchangers

Simplified computational fluid dynamics (CFD) models will be built with periodic and symmetric boundary conditions to simulate the complex inner structures of the heat exchangers. By optimising the fin structure, heat exchangers with high thermal-hydraulic performance and minimised size will be obtained.

Initial results:

Single-phase cooling

Based on our research on oblique fins for single-phase air and liquid cooling over the years, it can be concluded that secondary flows through the oblique cuts reinitialise the thermal and hydrodynamic boundary layers, thus ensuring a constantly developing flow, as seen in Figure

4.4. Besides that, secondary flows induce fluid mixing and more uniform temperature distribution. These bring about a significant reduction in wall temperature compared to straight channels at negligible pressure drop penalty.

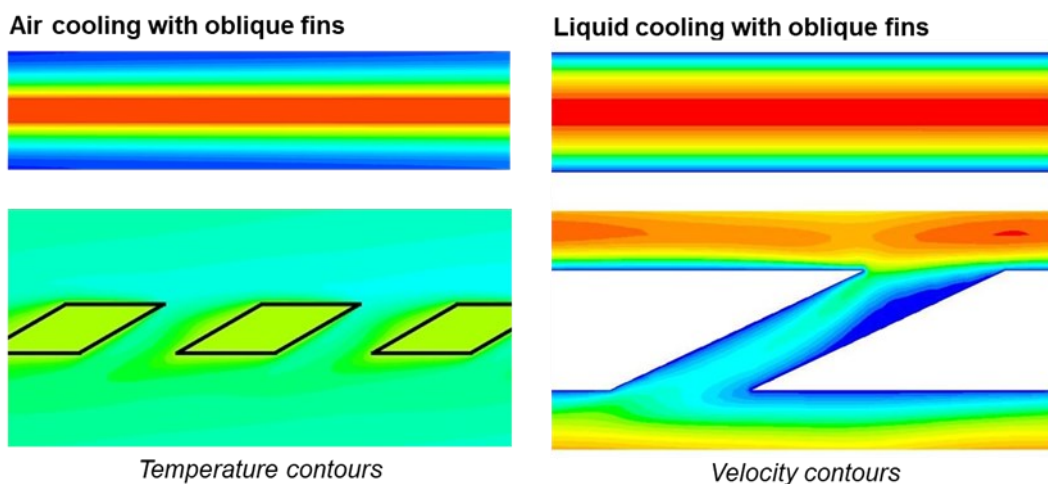


Fig 4.4: Temperature and velocity contours of flow through straight and oblique-fin microchannels.

Heat exchanger

Circular tubes are typically used in conventional and existing heat exchangers. However, there are always large wake zones behind the tubes which can significantly compromise convective heat transfer, as seen in Figure 4.5a. To address this issue, the shape of the tubes are changed from circular to elliptic (Figure 4.5b). Wake zones become smaller while effective heat transfer area increases. Friction drag is lower due to smaller

local acceleration effect by the smaller frontal area. To further enhance the performance, oblique tubes will be adapted to enhance the heat exchange. Initial results in Figure 4.5c show that wake zones are significantly reduced, which leads to reduced friction drag and enhanced cooling performance.

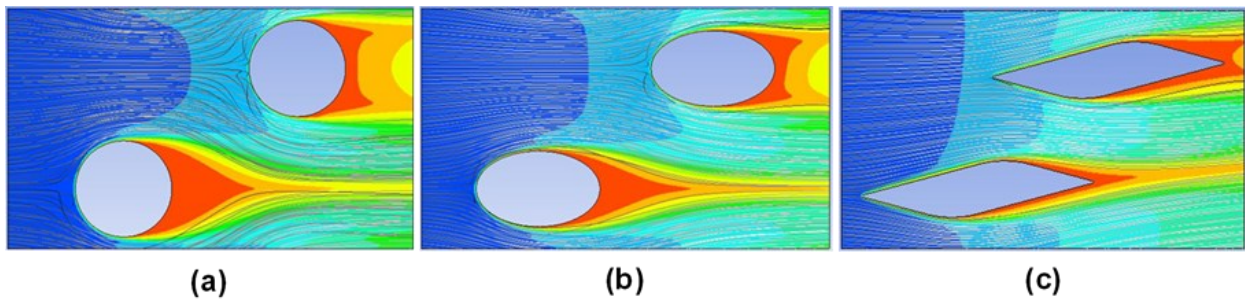
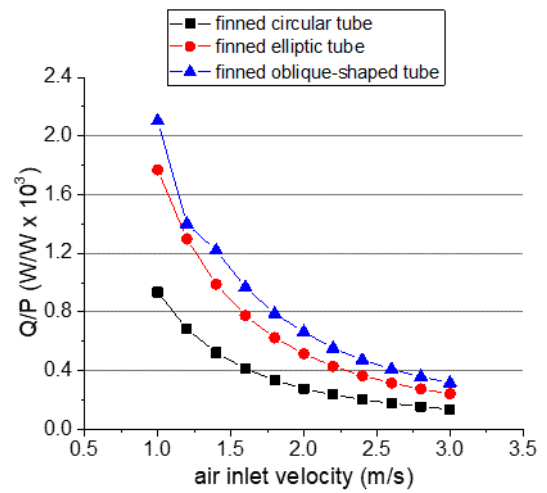


Fig 4.5: Temperature contours and velocity streamlines of (a) conventional circular tubes, (b) elliptic tubes and (c) oblique tubes.

A comparison of the overall cooling performance between circular tube, elliptical tube and oblique tube is given in Figure 4.6. As can be seen, the oblique tube has the highest heat transfer rate per unit pumping power compared to the rest for any given inlet flow rate. In other words, the oblique tube requires comparatively less pumping power to deliver similar heat exchange rate. This is more significant at low flow rates.

Fig 4.6: Overall performance comparison of the three tube heat exchangers.



Update on work package 4.4

Process system model for the J-Park Simulator

Objectives and methodology: Decision makers, fleet operators, and the general public do not have the expertise needed to operate the models in the previous WPs. However, the outcomes of the previous WPs are very useful knowledge for Singapore. For example, authorities must be in a position to apportion particulate emissions to the correct source (i.e. local factories? shipping? far-away forest fires?) and to be able to assess the PM environmental loading due to shipping in general, fuel switching, port operations etc. To this end, the results from the multi-dimensional CFD models of WP1-WP3 and the low-order engine models (WP1, WP2) will be implemented in the J-Park Simulator.

Initial results: The J-Park Simulator has been augmented to receive information from the AIS system, marking ship locations. This database provides on-line information on the ship's identity. Each ship is treated as a source of pollutant and its dispersion is modelled through ADMS (Figure 4.7). In the next steps of the project, the information about the type of engine and type of fuel used and the ship's speed and load will be used in low-order engine models to make realistic estimates of each ship's (i.e. each source's) emission. In addition, the reactivity of the near-plume will be considered. This will be a step-change in the accuracy at which ship emissions are estimated, which are now based only on averaged emission factors compiled over limited experiments spanning many different types of engines and fuels. The increased granularity of the prediction will allow more informed decision-making.

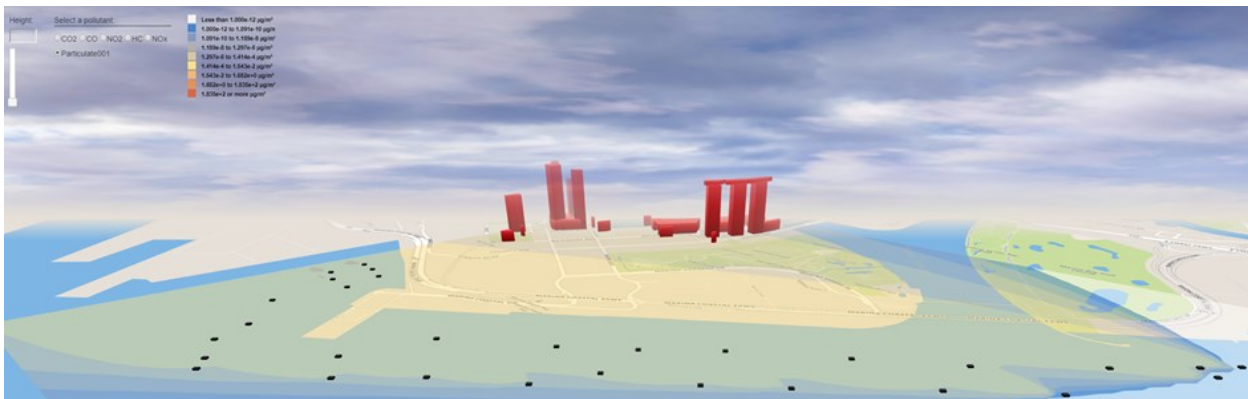


Fig 4.7: Example PM spatial distribution from ships in the Singapore area calculated by the J-Park Simulator. In this WP, the emission from each ship will be estimated based on its own engine and operating conditions, rather than the worldwide-averaged emission factors that are available at present, and introduced to the JPS.



IRP BB

BETTER BUSINESS: PATHWAYS TO INDUSTRIAL DECARBONISATION

The Better Business IRP acts as an incubator for ideas from all other IRPs and will support the acceleration and scaling of the technology outputs from the programme. It will examine different possible business models and compare the situation in Singapore with other important chemical clusters worldwide, engaging with stakeholders to identify the potential benefits and co-benefits of each technology arising from the programme.

IRP BB Principal Investigators:



Professor Steve EVANS
University of Cambridge



Professor S. VISWANATHAN
Nanyang Technological University



Assoc Professor Kenneth HUANG Guang-Lih
National University of Singapore



OVERVIEW

The Better Business IRP is new in Phase 2 and commenced in November 2018. Recruitment is nearly complete with two Research Fellows having joined so far, one in February and one in early April.

The IRP BB team is now working directly with all IRPs to prioritise their emerging technologies. IRP1 will offer the first two technologies to be analysed using first-cut IRP BB tools (including value mapping tools). The aim is firstly to identify better business models as well as better IP strategies for these two technologies.

Based on this learning, the IRP BB tools will be re-specified and novel development will begin. At the same time, IRP BB will examine other emerging technologies across C4T.

The group has also examined an industrial case on how business model innovation can be applied

to novel carbon reducing technologies in the process industry, reducing their time-to-market and improving value. These investigations lay fundamental bases for Work Package 1 (Business model innovation potentials).

Only one Research Fellow had commenced at the time of gathering information for this report, so this section will present a summary of the IRP instead of individual progress updates.

The work packages for IRP BB are:

WP1: Business model innovation potentials

WP2: Policy formulation, customer and industry perceptions

WP3: Future roadmap for industrial decarbonisation, including international comparisons.

Professor Steve Evans, PI
University of Cambridge

IRP BB progress update

Dr Wenjuan LI (Research Fellow, CARES) joined IRP BB in February 2019. After one month, she is now familiar with the achievements of Phase 1 and the research plans of Phase 2 across IRPs, as well as the basics of value mapping tools. She has also started learning game-theoretical approaches, which are expected to be useful when choosing business models and incentive mechanism design for supply chains in her upcoming research.

Although not published by IRP BB, the following paper demonstrates the conceptual basis for IRP BB inputs into C4T Phase 2:

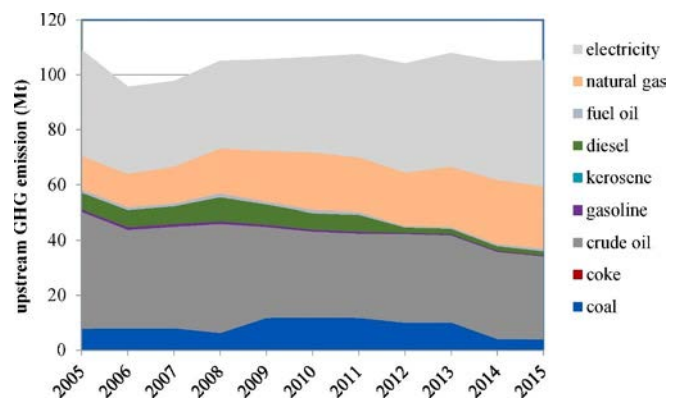
A hybrid scenario analysis for the selection of future greenhouse gas emissions reduction technologies in China’s oil and gas industry

Yuan Tao, Huifang Li, Zongguo Wen, Hongkun Chen, Wenjia Xu and Steve Evans

DOI: 10.1016/j.jclepro.2019.03.144

Abstract: Oil and gas provide approximately 22.7% of China’s total primary energy, but simultaneously absorbs 5% of that same energy. Increasing energy demands attributed to rapid industrialisation stand in contradiction to China’s stringent policies to reduce greenhouse gas (GHG) emission. The GHG emissions of China’s oil and gas industry was 377 Mt CO_{2-eq} in 2010, which was approximately 2.5 times higher than those of EU 27. Emission intensity in China is also much higher than that in EU 27. Accordingly, this study adopts a hybrid scenario analysis model to estimate the potential of GHG emission reduction of different technologies and policies in China’s oil and gas industry before 2030. The model was developed based upon a macroeconomic development model and a technology-based bottom-up system. The results indicate that GHG emissions will not peak before 2030 unless a strong

reduction policy scenario (SP) is implemented. Technologies that can favor reduce GHG emissions were ranked through a cost-benefit analysis with results showing that, in the short term, integrated optimisation of refining energy systems and torch optimising with associated gas recovery should be promoted, while, after 2020, ‘advanced’ technologies including carbon dioxide (CO₂) sequestration in saline aquifers and depleted hydrocarbon reservoirs, as well as CO₂ enhanced oil recovery can further reduce GHG emissions. However, significant improvements in R&D is a prerequisite for cost-effectively implementing these technologies.



GHG emissions from oil and gas exploration. International Energy Agency, 2005–2015.

Other activities and achievements

Prof. Steve EVANS (PI, CAM) gave a keynote presentation on industrial sustainability at Falling Walls 2018, held in Berlin on 8-9 November.

Prof. Evans was also a guest on CNBC’s TV series on Sustainable Energy, ‘How fashion, food and phones are embracing sustainability’.



Cambridge CARES

On 10 April 2019, **Prof. Steve Evans** led a team of researchers for a visit at Hwa Chong Institution, a Singapore junior college. Several Hwa Chong students heard a presentation about industrial sustainability, then visited a local factory to put their ideas into practice and search for ways that the factory could reduce its waste.





IRP JPS

THE J-PARK SIMULATOR

IRP JPS is an overarching research activity, with the ultimate purpose to show how research coming from each IRP affects the CO₂ output in Singapore and in particular the operations on Jurong Island. The research utilises the latest ideas from semantic web technologies and Industry 4.0 to integrate real-time data, knowledge, models and tools to fulfil objectives such as simulation and optimisation in cross-domain and multi-level scenarios. A main focus is to create superstructures of models contained within the developed ontologies for industrial parks to provide an accurate and fast-to-evaluate approximation of computationally expensive mathematical models for process industry plants in high dimensions.

IRP JPS Principal Investigators:



*Professor Markus KRAFT
University of Cambridge*



*Assoc Professor Raymond LAU Wai Man
Nanyang Technological University*



*Professor Iftekhar KARIMI
National University of Singapore*



OVERVIEW

With the start of Phase 2, the J-Park Simulator (JPS) has received a boost – a renewed thrust and focus in becoming an IRP in its own right. Riding on this wave, our efforts to ever expand the connected world represented in the knowledge graph of the JPS have progressed on several fronts. All these efforts have one underlying theme in common, namely to connect and integrate previously unrelated entities and demonstrate their interoperability by means of Semantic Web technologies. Over the past six months, we have developed new functionalities for the JPS to demonstrate its multi-domain and hierarchical capabilities, and to augment its degree of autonomy and intelligence.

For instance, we have developed and included ontologies for the chemical kinetic reaction mechanisms (OntoKin) and quantum chemistry calculations (OntoCompChem). With this inclusion, the JPS is now capable of describing both data and the semantics of the above-mentioned domains. In addition to the ontologies, we have also developed use cases that utilise these ontologies. In one of the use cases, we have included the possibility for the user to select from two different domains i.e. power plant and ship, a reaction mechanism and query for its details from the OntoKin knowledge base in order to execute an engine combustion simulation using the SRM Engine Suite. The SRM Engine Suite simulates the exhaust gas emissions e.g. carbon monoxide, nitrogen oxides, and soot from the engine which is subsequently being used in conjunction with the

surrounding buildings and weather data for the simulation of its atmospheric dispersion. In another use case, a semantic web service named “MolHub”, which utilises both Ontokin and OntoCompChem, was developed and integrated into JPS to establish semantic interoperability between different tools used in quantum chemistry and thermochemistry calculations. Finally, we have been able to add chemical kinetic reaction mechanisms as well as first-principles quantum calculations for chemical species to the JPS knowledge graph, and establish links between species and their corresponding quantum calculations. This is an important first step towards resolving inconsistencies in rate and thermodynamic data found in the literature, and towards building and using chemical models in other contexts within JPS.

We have also extended the semantic web service composition prototype with blockchain-based smart contracts functionalities to enhance the trustworthiness of the records and automate the payment process upon fulfilment of specified payment conditions.

We are currently further developing OntoKin and OntoCompChem to increase the number of chemical kinetic reaction mechanisms and species in the knowledge base. We are also investigating the concept and architecture for “parallel world”, which is an imperative step in facilitating what-if scenario analysis. We intend to develop a prototype for this concept and architecture based on integrating an agent that identifies the optimal number and locations for modular nuclear power plants and the existing electrical grid models.

Professor Markus Kraft, PI
University of Cambridge

Update on work package JPS.1

Big data — sensors and data modelling

Dr **Andreas EIBECK (Computer Scientist, CARES)** is investigating a framework to enable agents to execute several parallel optimisation strategies or to simulate cross-domain scenarios with varying initial assumptions i.e. what-if scenarios analysis. Agents are applications and services that utilise semantic technologies and are accessible on the World Wide Web. This research is necessary as the agents currently update the knowledge graph directly and hence any change will be visible to all other agents immediately. While this is suitable for circumstances where agents’ actions result in changes in the states of the real-world entities, e.g. when components of cyber-physical systems read and process sensor data and provide signals to the actuator, the design has to be further developed to facilitate JPS’ scenario analysis functionality. Dr Eibeck has elaborated a concept and implemented a first prototype that enables the agents to collaborate in a “secured portion” of the knowledge graph without interfering with other agents or impacting the “real” world.

Aravind DEVANAND (PhD student, NUS) has been extending and refining the domain ontology for power systems, *OntoPowSys*, in collaboration with Dr Rémy RIGO-MARIANI (former CARES Research Fellow and current colleague at ERI@N, NTU) and Leonardus Kevin ADITYA (Project Officer, NTU). *OntoPowSys* was developed in Protégé using the OWL language and is capable of representing knowledge in the power system

domain. Aravind is currently in the process of testing the ontology, which involves the following steps. Firstly, inconsistencies in the ontology schema or the T Boxes are identified using *HermiT*, a description logic-based reasoner. A total of nine inconsistencies have been identified and rectified accordingly. Secondly, inconsistencies in the instances or the A Boxes are also identified using *HermiT*. The identified inconsistencies are rectified accordingly. Lastly, the ontology was validated, i.e. evaluating the inferences from the ontology with the help of an electrical engineer, Gourab KARMAKAR (Research Associate, NTU) and Dr Nenad KRDZAVAC (Senior Software Developer, CARES). Aravind is currently writing up a paper on this work.

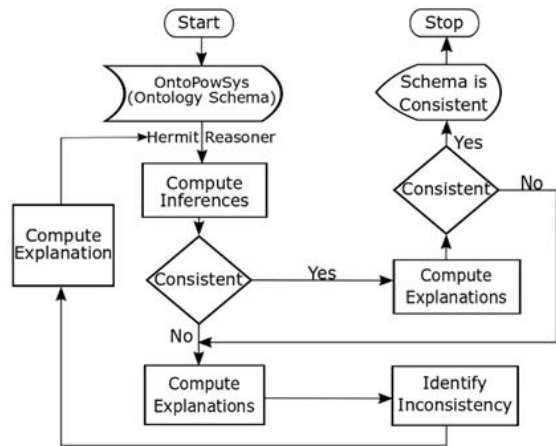


Fig. 5.1: Consistency evaluation procedure for *OntoPowSys* schema.

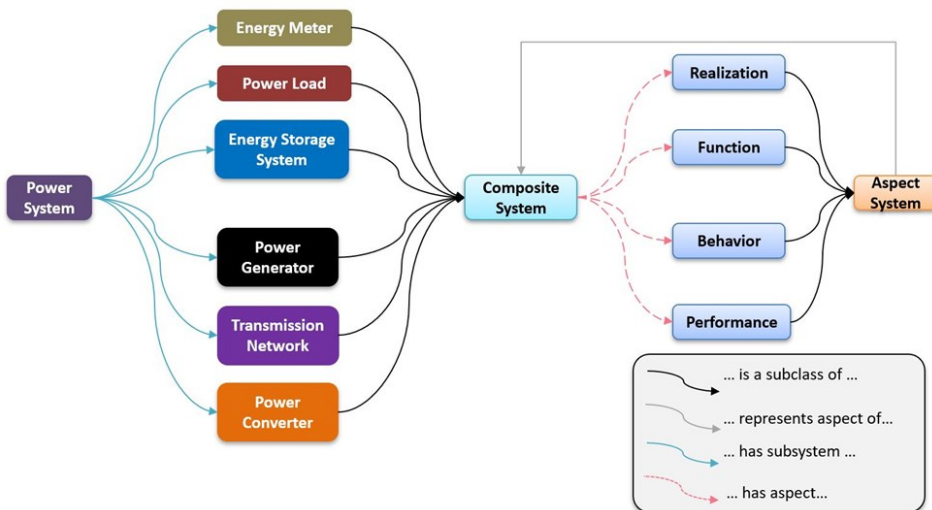


Fig. 5.2: Major classes defined in the *OntoPowSys* ontology.

Update on work package JPS.2

Surrogate models and superstructure

Changmin YU (PhD student, CAM) who is supervised by Dr Sebastian MOSBACH (Senior Research Fellow, CAM) has been studying machine learning-based surrogate modelling techniques for diesel engine emission simulations. He investigated a state-of-the-art machine learning algorithm, deep kernel learning (DKL), and implemented it as a surrogate for modelling the diesel engine emission. This research involves the following steps: The input data is first fed into a fully-connected neural network. Following that, the neural network will extract low-dimensional features that can subsequently be fed into the Gaussian process for regression. The training is through gradient descent, using the partial derivatives of the posterior marginal likelihood with respect to the kernel parameters and network weights through standard backpropagation.

This approach combines the ability of neural networks in extracting features of higher abstraction and the ability of Gaussian processes in fitting any functional form due to the fact that its adaptive basis function size is infinite. Computer experiments have shown that DKL outperforms deep neural networks and Gaussian processes separately, as well as existing surrogate modelling methods such as High-Dimensional Model Representation (HDMR) while maintaining the

computational time at a reasonable scale. Changmin will be developing more surrogate modelling techniques and translating them into agents that will subsequently be integrated into JPS. He will also be investigating a framework to automate the process of surrogate modelling of physical systems such as diesel engine, which could potentially replace the highly time-consuming detailed physical models for tasks such as emission modelling and engine calibrations.

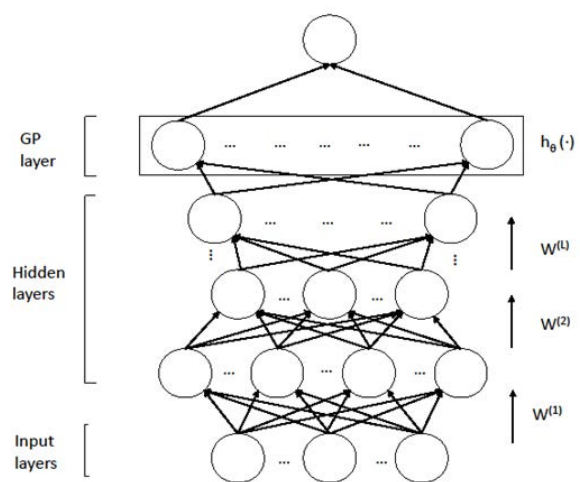


Fig. 5.3: Graphical representation of a deep kernel learning method.

Update on work package JPS.3

Implementation

Dr Andreas EIBECK (Computer Scientist, CARES) is responsible for the overall architecture of the JPS and has been working on several steps to drive the JPS forward. He is heavily involved with supporting the JPS team concerning questions of software design and non-functional requirements such as performance and scalability. Dr Eibeck wrote a paper that describes the main principles of JPS. In this paper, he describes how JPS knowledge graph utilises modular and reusable domain ontologies to store and link instances and data values that are described semantically. The knowledge graph can be distributed over different web nodes and forms the lower data

layer within the JPS software architecture. The upper layer consists of agents that implement functionalities, collaborate with each other and can read from and write to the knowledge graph. The interoperability between agents in cross-domain scenarios has been illustrated with a comprehensive air pollution scenario.

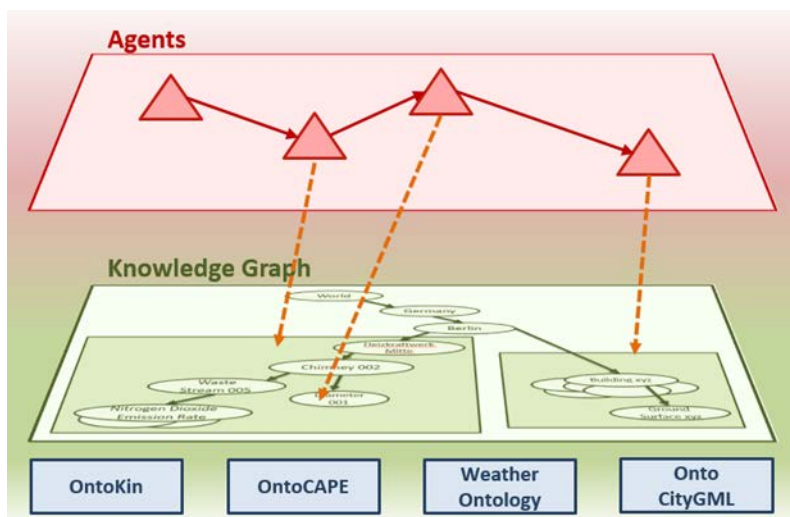


Fig. 5.4: Main principles of the J-Park Simulator (JPS): a) modular domain ontologies (blue), b) distributed knowledge graph (green and blue), c) agents (red) operating on the knowledge graph and interacting with each other.

Dr Andreas EIBECK

Dr Jethro AKROYD (Senior Research Fellow), Dr Sebastian MOSBACH (Senior Research Fellow) and Dr Feroz FARAZI (Research Associate), all University of Cambridge, have developed an ontology, called OntoKin, for capturing both data and the semantics of chemical kinetic reaction mechanisms by using concepts and properties extracted from domain experts and published resources. These chemical kinetic reaction mechanisms can be applied to simulate and understand the behaviour of chemical processes, for example, the emission of pollutants from internal combustion engines.

Dr Farazi used an ontology development methodology to assist in producing the semantic model of the mechanisms. As part of the development methodology, the ontology is formally represented using OWL, assessed by domain experts and validated by applying a reasoning tool.

Dr Akroyd has actively been involved in the development as a domain expert by contributing to the selection of ontological concepts, object properties and data properties. He has also validated the ontological modelling of reaction mechanisms as concept-concept relations. These relations can be classified into three types: the subsumption relation (i.e. is-a), part-of relation (i.e. part-whole) and user-defined relations (e.g. belongs-to and participates-in). Dr Akroyd has also contributed to the cross-validation of labels (names) and definitions of concepts and properties.

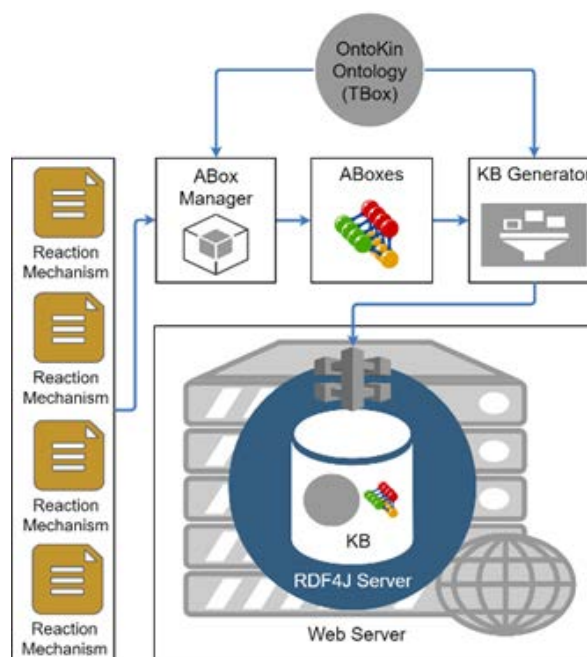
Dr Mosbach has been involved in validating the semantic correctness of the modelling of species,

reactions and phases (i.e. gas-phase, bulk-phase and site-phase).

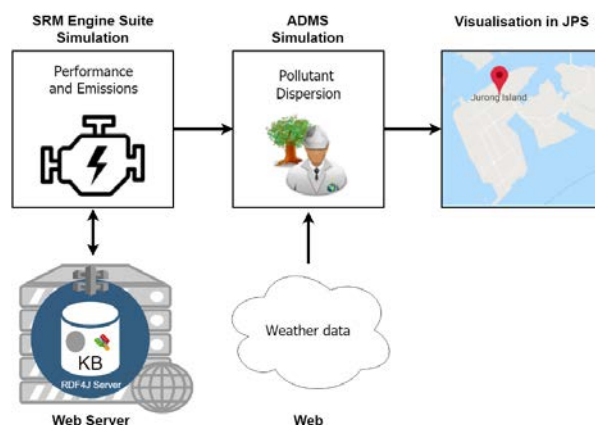
Dr Farazi has developed a tool, shown in Figure 5.5, to automate the assertion process. The toolset includes an ABox Manager that uses the OntoKin ontology or TBox and OWL API to convert CHEMKIN mechanism files to OntoKin instances or ABoxes and a Knowledge Base (KB) Generator that imports the OntoKin TBox and ABoxes into the KB. The KB was deployed using the RDF4J triple store. Dr Mosbach is instrumental in deploying the OntoKin KB using the RDF4J triple store and making URLs of all published OntoKin resources including the TBox and ABoxes resolvable. The current version of the KB has been developed by integrating OntoKin with the ontological representation of 34 publicly available mechanisms obtained from research organisations including universities and scientific laboratories. The largest mechanism contained approximately 3,000 species and 19,000 chemical reactions. The smallest mechanism, on the other hand, contained as few as 14 species and 33 reactions. The mechanisms were analysed from the perspective of the level of granularity and the parametric conditions. The level of granularity relates to whether it is a detailed mechanism that attempts to describe the full chemistry of a system, or a reduced mechanism that attempts to mimic the behaviour of the full chemistry under a restricted set of conditions. The parametric conditions relate to whether different mechanisms describe things that purport to represent the same physics in the same way. The development of the KB allows

queries and reasoning to be performed across mechanisms. The domain experts were consulted to identify the types of queries of interest. The questions ranged from being as simple as requesting all the mechanisms containing a specific species or mechanisms developed by a specific organisation to much more complex questions. For example, requesting all mechanisms which have inconsistent rate models for the same reaction. In this case, sameness is defined in terms of the equality of the reactants and products, but in general, the definition of sameness could be more extensive.

Fig. 5.5: The toolset for generating the OntoKin Knowledge Base.



Dr Farazi has also developed an API, shown in Figure 5.6, using the RDF4J Model API. The API takes advantage of the choice to represent mechanisms using ontologies (in any of the Semantic Web formats including OWL and RDF). The API enables a software called “SRM Engine Suite” to programmatically import mechanisms by sending a request with the Internationalised Resource Identifier (IRI) of the mechanism to the KB. The KB responds by returning the RDF representation of the mechanism, which can be converted to a form that is readable by the SRM Engine Suite.



NG Wei Ern (Software Developer, CARES) and Leonardus Kevin ADITYA (Project Officer, NTU) have extended the air pollution scenario to include usage of OntoKin and SRM Engine Suite. This activity involves developing an agent for SRM Engine Suite, ontology for the domain of ships, and extending the Atmospheric Dispersion Modelling System (ADMS) model to accommodate multiple emission sources and types of pollutant. The user can select from two different domains i.e. power plant and ship, a reaction mechanism and query for its details from the OntoKin KB in order to execute an engine combustion simulation using the SRM Engine Suite. The SRM Engine Suite simulates the exhaust gas emissions e.g. carbon monoxide, nitrogen oxides, and soot from the engine which is subsequently being used in conjunction with the surrounding buildings and weather data for the simulation of its atmospheric dispersion.

Fig. 5.6: The SRM-ADMS use case.

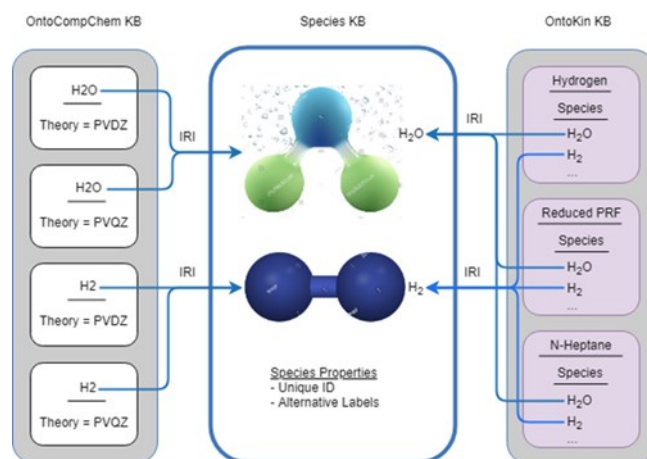


Fig. 5.7: Dispersion profile for atmospheric dispersion simulation of 30 ships with arbitrary cruising positions around waters surrounding Singapore at a height of 30 m.

Dr Nenad KRZAVAC (Senior Software Developer, CARES), Dr Akroyd and Dr Mosbach have developed an ontology, called "OntoCompChem", for representing the semantics of quantum chemistry calculations by using the semantics of ComChem convention of Chemical Markup Language (CML) and by extending the Gainesville Core (GNVC) ontology. They have also developed a novel "MolHub" web service in order to establish semantic interoperability between different tools used in quantum chemistry and thermochemistry calculations, and this web service has been integrated into JPS. Dr Krdzavac implemented a hydrogen mechanism semantic web service that utilises the developed OntoCompChem and other ontologies such as OntoKin, Species and OntoAgent. A selected set of hydrogen mechanisms consisting of about ten selected hydrogen species is used to demonstrate how the semantic web service functions. Firstly, the quantum calculations are uploaded using MolHub. Molhub will parse the quantum calculations and automatically populate the OntoCompChem ontology with the parsed data and deploy the generated ontologies into the RDF4J triple store. For this web service, the HTTP request con-

Fig. 5.8: An illustration of how the agent-based framework deals with multiple mechanisms, the automation of quantum calculations and the creation and modification of knowledge graph.

tains a parameter called "gaussian", which is an instance of the OWL class "Gaussian" in the OntoCompChem ontology. Whenever a HTTP request is issued, the web service will run a set of SPARQL queries on the RDF4J triple store mentioned above. The queries will return all information about quantum calculations that are utilised as inputs for computing NASA polynomials. The results are stored as JSON files which are subsequently being used by a python script for calculating NASA polynomials. The output from the calculation is a JSON file which is then converted into ontology file that represents a set of individual assertions (A Boxes) of OntoKin ontology by using an API developed by Dr Farazi. The resulting OWL file is stored automatically into RDF4J triple store.



ZHANG Chuan (PhD student, NTU) has developed detailed surrogate models for estimating carbon emissions from various types of power plant. Together with Wei Ern and Kevin, he translated these surrogate models into agents and integrated them into JPS. Chuan, in collaboration with Dr Rigo-Mariani, has formulated a novel industrial combined heat and power cogeneration optimisation problem by implementing a Combined Cycle Gas Turbine model and an efficient power dispatch strategy based on minimising CO₂ emissions. In this problem formulation, the power grid is represented by 208 buses, 219 branches and the thermal network is represented by 14 nodes and 14 steam pipes. A distinction was made between pure electrical consumers and

consumers with both thermal and electrical loads. Heavy consumers (e.g. oil refineries) are assumed to have their own steam supply while the other thermal consumers are assumed to be aggregated in mutualised heating districts. Losses are computed based on the cables/pipes characteristics and the estimated distances between them. The results indicated significant improvements compared to when cogeneration units are not controllable (i.e. when priority is given to electrical output). These improvements become more pronounced when higher heat load levels or dirtier additional boilers are considered. The observations also revealed the necessity to size the steam pipes appropriately as the lower bound for the heat flow is the binding constraint in most cases.

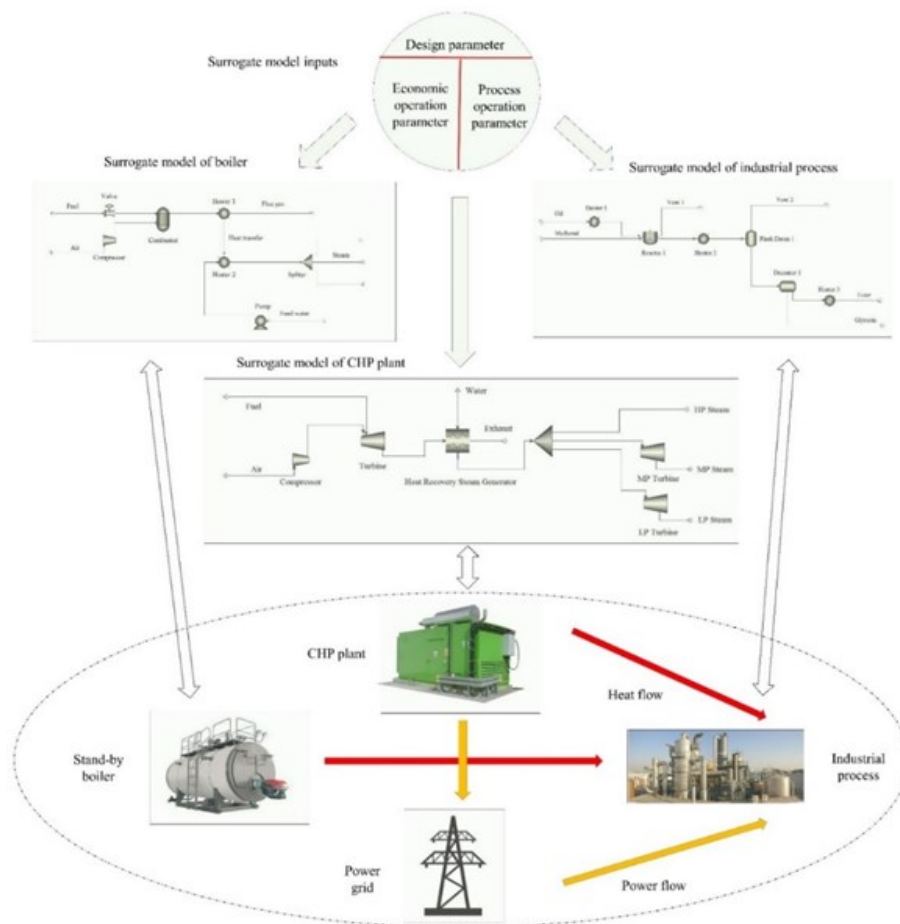


Fig. 5.9: Surrogate model-based optimisation framework for industrial cogeneration system.

ZHANG Chuan

Aravind DEVANAND (PhD student, NUS) has refined a mathematical optimisation model capable of identifying optimal location for modular nuclear power plants in a region. The capabilities of the model were demonstrated by conducting a case study in JPS. The model has been published in the Computers and Chemical Engineering journal. Aravind is currently working on integrating the results from the model with the electrical network in JPS. This work is conducted in collaboration with Dr Eibeck, Kevin and Gourab. Kevin is responsible for integrating and providing the models with semantics based on the refined ontologies. In the integrated model, the modular nuclear power plants model will provide the optimal locations and capacities for the modular nuclear power plants which will subsequently be utilised by the optimum power flow (OPF) model developed by Dr Rigo-Mariani to optimise the power flow throughout

the electrical network based on the electricity supply and demand. This use case will serve as a demonstrator for the “parallel world” concept developed by Dr Eibeck as mentioned in work package JPS.1.

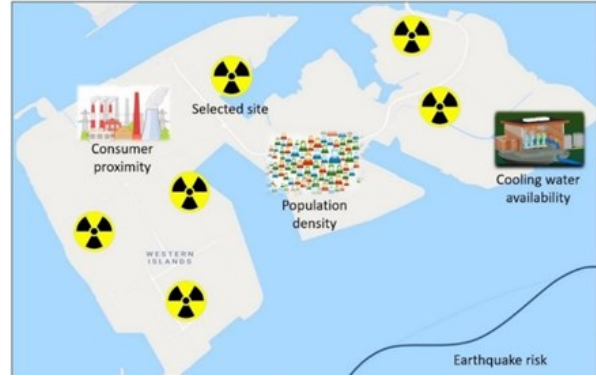


Fig. 5.10: Graphical abstract for the modular nuclear power plants model.

Aravind DEVANAND

ZHOU XiaoChi (Software Developer, CARES) has developed an agent composition framework based on semantic web technologies that can create schemes for agent coordination in an automated and dynamic manner, hence increasing the efficiency and flexibility of coordinating agents. This framework is based on an ontology, called OntoAgent, which is an extension of the Minimal Service Model (MSM) ontology. With OntoAgent, agents can be precisely interpreted by machines to facilitate automation of processes such as agent discovery, agent composition and agent execution. XiaoChi also developed a prototype for semantic agent discovery, which is based on SPARQL queries, that selects agents according to their input and output parameters. This prototype adopts a graph-based forward-chaining algorithm for combining the agents. Ontology lookup service (OLS) is also implemented in the framework to convert natural language terms into ontology Uniform Resource Identifiers (URIs) to facilitate the user’s definition of composite agents. In addition, XiaoChi has introduced blockchain-based smart contracts

within the agent composition framework to build a trust and financial layer for the interaction between agents. Due to the tamper-proof and distributed nature of blockchains, the logic of the smart contracts cannot be manipulated and no party can intervene with the execution in their favor. XiaoChi has implemented the features of smart contracts in the evaluation of agent performance, payment and compensation, and reputation management, thus forming an automated and decentralised agent marketplace. The implementation is based on the Ethereum blockchain framework, while the smart contracts are developed with Solidity language, and the smart contracts are published on the Rinkeby network. All the invocation of agents are via Oraclise services implemented on smart contracts, such that the raw data of invocation e.g. response time and outputs are in the control of the smart contracts, which is an unbiased and trustworthy party. Consequently, the smart contracts are able to compute the performance score based on the invocation data.

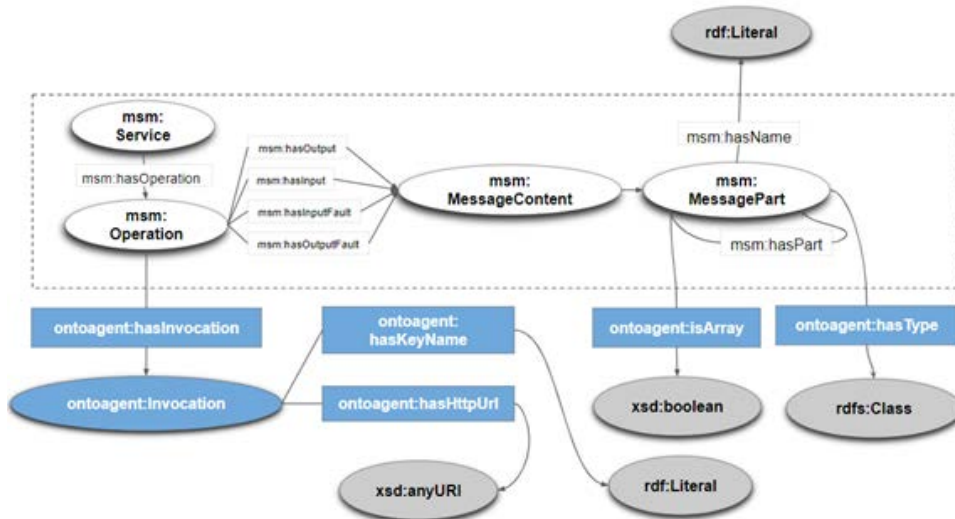


Fig. 5.11: Classes and properties of OntoAgent.

Fig. 5.12: Semantic web service composition with performance evaluation.

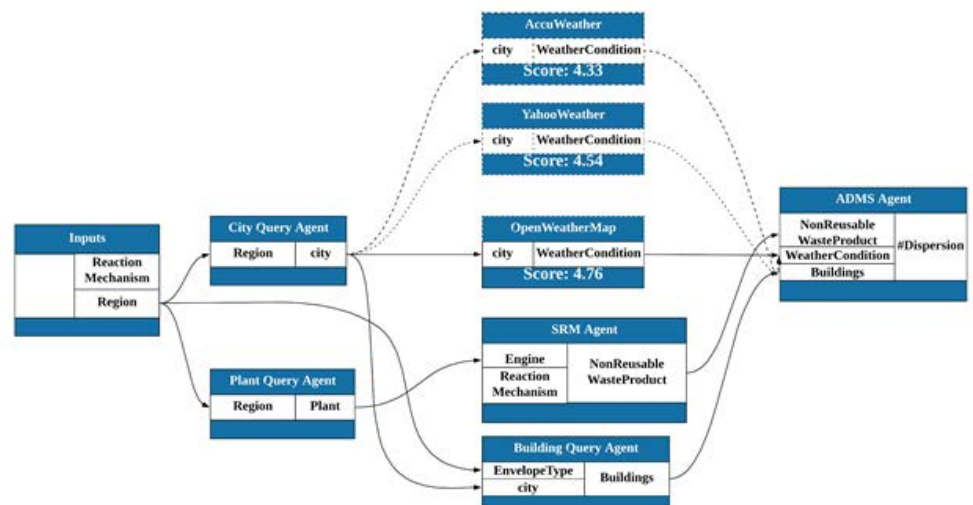


Fig. 5.13: Smart contract-based agent marketplace.

ZHANG ShaoCong (Software Developer, CARES) is currently researching ontology matching with the use case of integrating semantic data for power plants domain from dbpedia with the relevant data available in JPS. She has explored an open source framework, called 'AgreementMakerLight', and is in the process of improving its suitability and accuracy for general automated data integration.

Khamila Nurul KHAQQI (PhD student, NTU) has been doing follow-up research on the blockchain enabled emission trading scheme. The use of blockchain technology as well as the introduction of reputation system to govern the trade in its market creates a unique system and architecture. As such, Khamila examines the reliability of the system that she has designed. She defines the reliability as a consistent performance of the system; that the shift in transaction prices as a result

of the introduced measure is independent of the market condition. The price level and market depth are identified as specific factors that may influence the state of the market and therefore eventually the transaction prices. The price level is a concern due to the fact that emission permit price's trend is different in different emission trading market and the way the trade is organised is dependent on the proposal price's nominal value. The market depth refers to the number of

buyer or seller participating in the market. The number of participants influences the offer price's choice and spread, and eventually the transaction price. Since we discriminatorily limit the access to buying and selling offer by percentage of participants, the resulted transaction price can be very different. Khamila examined these aspects using Monte Carlo simulation to ensure that the outcome is similar and independent of the stated factors.

Update on work package JPS.4

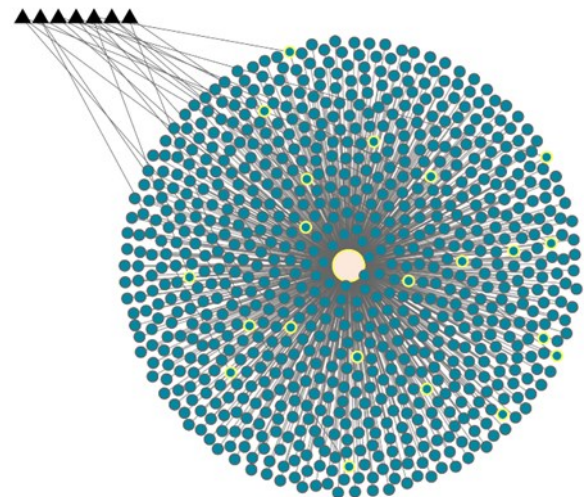
Model analysis and visualisation

ZHANG ShaoCong (Software Developer, CARES) has developed a general framework that can be used to visualise the multi-domain data in JPS. The visualisation framework displays ontology instances as nodes and relations (properties) as lines connecting the nodes. To facilitate navigation, the ontology instances are displayed level by level, originating from a specific head node. ShaoCong has also developed two versions of the visualisation framework that are optimised for different scenarios. In one of these versions, the framework is optimised for performance by querying the knowledge base in one go. However, this design is unsuitable in scenarios where the number of entities involved in the query is huge and hence rendering it almost impossible to either query or display them using existing computational resources. Consequently, in another version, the framework is modified to send backend queries in a request-by-request basis, i.e. one request for each instance. The query request will

only be processed when the user is trying to expand the node of interest. This design eliminates the problem described above by allowing a number limit to be placed on each query. ShaoCong has also enhanced the visualisation framework with an "import" function to display the links between class definition and ontology instances. In addition, she also developed a mechanism to indicate the nodes' activity status, i.e. a node will "blink" when it undergoes modification.

ShaoCong, Wei Ern and Kevin have developed a prototype for visualising agents' activity in real-time by displaying the operating relationship between the agents (represented by triangles) and the ontology instances (represented by nodes).

Fig. 5.14: Visualisation of activities of seven agents acting on nodes representing power plants.



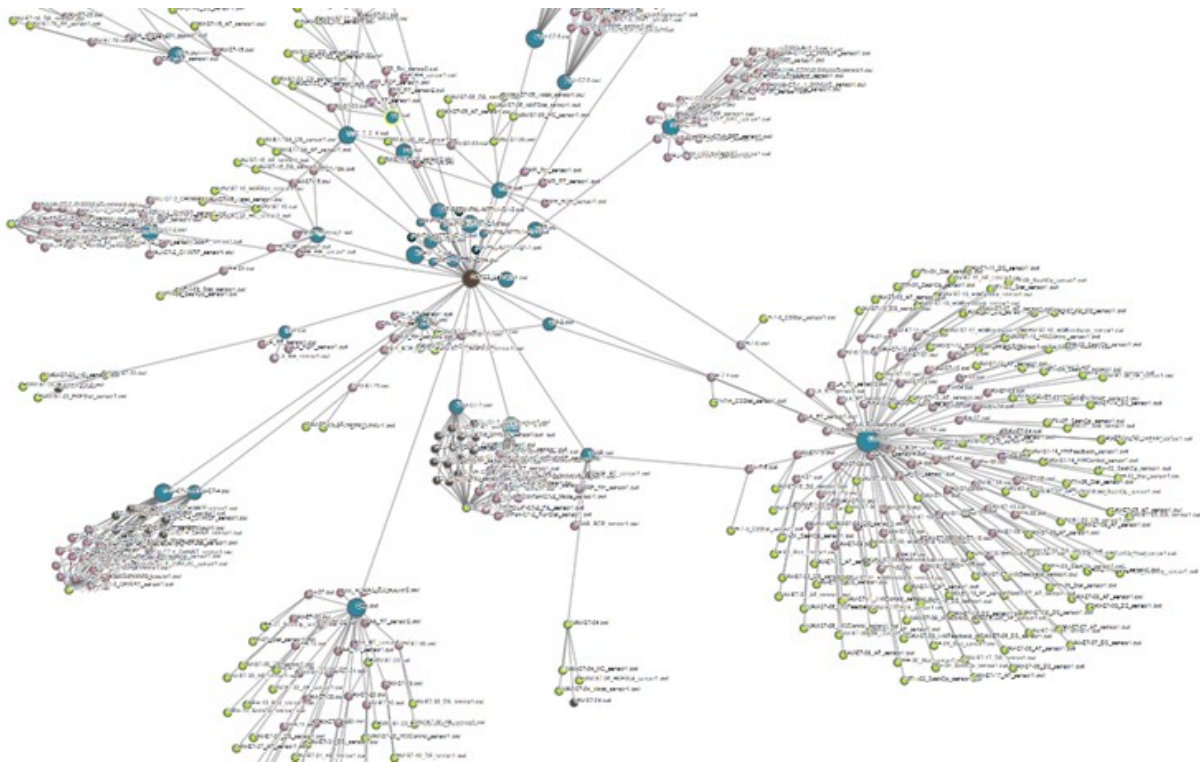


Fig. 5.15: Visualisation of the Building Management System (BMS) of the CARES Laboratory.

NG Wei Ern (Software Developer, CARES) has developed the visualisation for the SRM-ADMS-Ship agent by utilising HTML, CSS, JavaScript, and OSMBuilding.js, a front-end JavaScript package which provides the functionality of rendering

3D building models on the world map. He also implemented the back-end of the agent using Java and Python which is subsequently being deployed on Tomcat web container.

Scientific output

The following are the CREATE-acknowledged publications generated by IRP JPS during the reporting period, excluding those already featured in the Scientific Highlights section on page 13.

A combined cycle gas turbine model for heat and power dispatch subject to grid constraints

Rémy Rigo-Mariani, Chuan Zhang, Alessandro Romagnoli, Markus Kraft, K. V. Ling and Jan M. Maciejowski, *IEEE Transactions on Sustainable Energy*

DOI: 10.1109/TSTE.2019.2894793

Abstract: This paper investigates an optimal scheduling method for the operation of combined cycle gas turbines (CCGT). The objective is to minimise the CO₂ emissions while supplying both electrical and thermal loads. The paper

adopts a detailed model of the units in order to relate the heat and power outputs. The grid constraints as well as system losses are considered for both the electrical and thermal systems. Finally, the optimal power dispatch lies on the hybridization of a Mixed Integer Linear Programming (MILP) scheduling with a greedy search method. Different sets of simulations are run for a small 5-bus test case and a larger model of Jurong Island in Singapore. Several load levels are considered for the heat demand and the impact of the steam pipe capacities is highlighted.

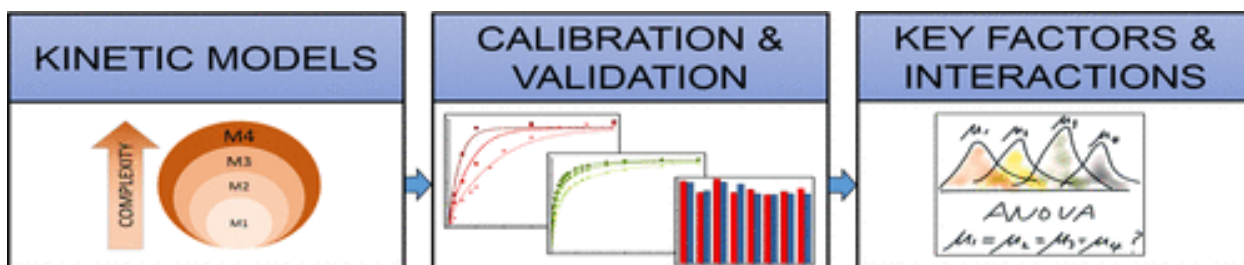
Practically useful models for kinetics of biodiesel production (combined with IRP3)

Pulkit Chhabra, Sebastian Mosbach, Iftekhhar A. Karimi and Markus Kraft, *ACS Sustainable Chemistry & Engineering*

DOI: 10.1021/acssuschemeng.8b05636

Abstract: We develop four kinetic models of varying complexity for biodiesel production. The models incorporate both transesterification and saponification, thereby making them practically applicable. We then propose an iterative parameter estimation algorithm to identify a prefixed number of significant rate constants via sensitivity analysis and estimate their kinetic parameters (A and ΔE) using nonlinear

regression. Using experimental data on eight different oils, two alcohols, and two catalysts, we show that our models accurately predict the dynamic concentration profiles of various species during the transesterification of oil. Furthermore, we demonstrate the applicability of the best model (based on the values of Mean Absolute Error, Root Mean Square Error, and Akaike Information Criterion) for 11 additional experiments by predicting the final biodiesel properties with significant accuracy. Finally, using N-way ANOVA, we identify the choice of oil, alcohol, and catalyst as the most significant input factors followed by the operating conditions of the reactor.



Other activities and achievements

Prof. Markus KRAFT (PI, CAM) visited Hong Kong to attend the Green Life Asian Innovation Forum on 16 February, and gave a keynote presentation on the J-Park Simulator. Prof. Kraft spoke about how carbon emissions can be reduced through a combination of increased energy efficiency and new business models, using Singapore as an example. While travelling, Prof. Kraft



also met several members of faculty at the University of Hong Kong.

Prof. Kraft has also been elected to the board of the new ASEAN-Pacific chapter of MindSphere World, an initiative run by Siemens. The MindSphere alliance brings together industrial and higher education members with the purpose of forming and developing an Industrial Internet of Things community.

LIM Mei Qi (Research Project Manager, CARES) prepared and coordinated the presentation of JPS to Pro Vice-Chancellor of Newcastle University, delegates from Federal Ministry of Education and Research (BMBF), Institute of Chemical & Engineering Sciences, Senior R&D Manager of Sembcorp Marine Ltd and Global Young Scientists Summit. In addition to IRP JPS, Mei Qi also managed the research collaboration (Digital Assistance For The Process Industry) with Siemens.

Prof. Kraft at the Green Life Innovation Forum in Hong Kong.



eCO₂EP

CARBON CAPTURE AND UTILISATION USING A TABLE-TOP CHEMICAL FACTORY

This is CARES' first Intra-CREATE project, which aims to develop a "table-top chemical factory" that uses electrochemical processes to convert CO₂ into ethylene or to 1-propanol – two molecular products widely used in the chemical industry. Earlier research carried out at CREATE has demonstrated that CO₂ molecules can be transformed into hydrocarbons through the application of electrocatalysis. eCO₂EP's research studies the viability of scaling CO₂ reduction processes, including techno-economic evaluation of the use of off-peak renewable electricity in areas with excess capacity. The project will allow the exploration of a new energy-chemistry solution for a more sustainable future.

eCO₂EP Principal Investigators:



Professor Alexei LAPKIN
University of Cambridge



Professor Joel AGER
University of California, Berkeley



OVERVIEW

The eCO₂EP project is currently in its months 12-18. Recently the new mass-spectrometer system (PTR-MS) has been installed and is currently being commissioned. Excellent results were obtained with improving GDE long-term stability and the work on new catalysts is progressing well. The modelling team has developed a simple 1-D model and work on micro-kinetic model is in full swing. The work on products separation is also progressing well, with a set of promising ad-

sorbent materials identified through a collaboration with Dr David Fairen-Jimenez at University of Cambridge.

Professor Alexei Lapkin, PI
University of Cambridge

Professor Joel Ager, PI
University of California, Berkeley

Update on work package 1

New catalyst discovery and characterisation

Dr Yubo CHEN (Research Fellow, NTU), has been exploring catalysts for water oxidation in acidic electrolyte, in particular those containing iridium, which is the only element with a high resistance to the acid corrosion during water electrolysis. However, iridium is a rare element. To optimise the activity of iridium on a per-atom basis, Dr Chen has designed and tested a pseudo-cubic perovskite ($\text{SrCo}_{0.9}\text{Ir}_{0.1}\text{O}_{3-\delta}$). This work has been published in a recent paper which is featured in the scientific highlights on page 18—“Exceptionally active iridium evolved from a pseudo-cubic perovskite for oxygen evolution in acid”.

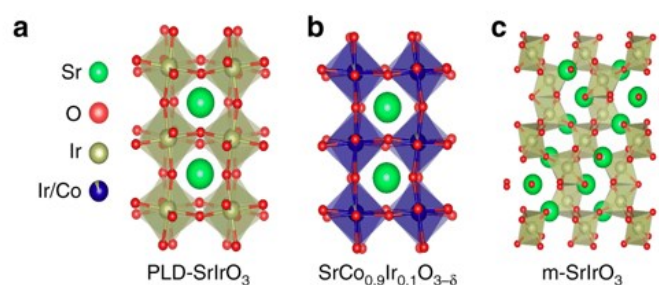


Fig. 6.1: Crystal structures of **a** PLD-SrIrO₃, **b** pseudo-cubic SrCo_{0.9}Ir_{0.1}O_{3-δ}, and **c** m-SrIrO₃.

Dr Yubo CHEN

Dr Guanyu LIU (Research Fellow, NTU), has been working on copper-based bimetallic nanocatalysts for electrochemical carbon dioxide reduction. The effects of different metals (e.g. Ag) on the selectivity of copper catalysts for electrochemical CO₂ reduction have been investigated. The ratio between copper and another metal was optimised to improve the faradaic efficiency for ethylene production. In addition, he also developed CuO-based catalysts with a non-metal dopant using a scalable gas-fed flame synthesis method. The amount of dopant in copper oxide was tuned by adjusting the feed rate of the precursor containing dopant source. It was discovered that the dopant could suppress hydrogen evolution and facilitate carbon dioxide reduction reaction.

Besides this, photoelectrochemical CO₂ reduction performance using semiconductor-based photocathodes was investigated. Both planar and nanopillar photocathodes modified by various interfacial engineering methods were tested. Both the selectivity and activity for photoelectrochemical CO₂ reduction were influenced by the interfacial

property and morphology of the semiconductor. Dr Liu also completed and submitted a review article entitled “Research Advances towards Large-Scale Solar Hydrogen Production from Water” to the journal *EnergyChem* with Yuan Sheng, Joel W. Ager, Markus Kraft and Rong Xu.

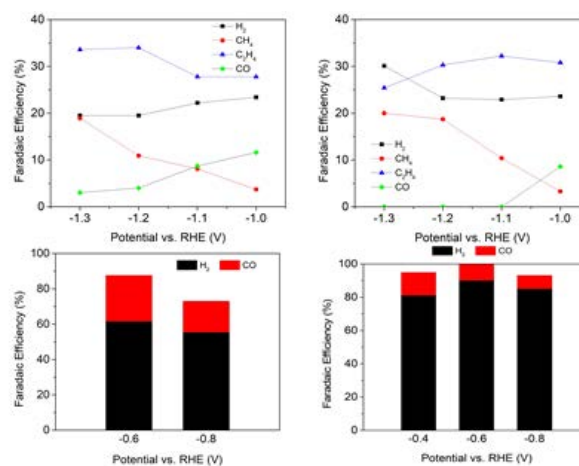


Fig. 6.2: Electrochemical and photoelectrochemical CO₂ reduction performance of the synthesised catalysts.

Dr Guanyu LIU

Dr Divya NAGARAJU (Research Fellow, NUS), has been working on developing catalysts for the utilisation of CO₂ as chemical feedstock for value added products which further can pave the path for mitigating increased greenhouse gas. Electrochemical conversion of CO₂ is the most efficient way for producing industrial feedstocks. However, producing higher hydrocarbon ($\geq C_2$) gaseous and liquid products with high selectivity, high faradaic efficiency and low activation over potential is still a challenge. She is focusing on developing an appropriate design of the catalyst with suitable morphology, that can address the challenge by producing $\geq C_2$ products.

Most recently, Dr Nagaraju has successfully developed boron doped Cu catalyst through pulsed laser deposition and oxide derived dendrite like Cu catalyst through electrochemical synthesis. In one of her works, the dendrite like structures of Cu exhibited a faradaic efficiency of 48% for $\geq C_2$ products, while ethylene at 33% and ethanol at 11% faradaic efficiency. These catalysts also show high selectivity for C₂ products. She is further focusing on increasing the stability and long time performance of these catalysts. The mechanism involved shall be further investigated both by experimental and theoretical studies.

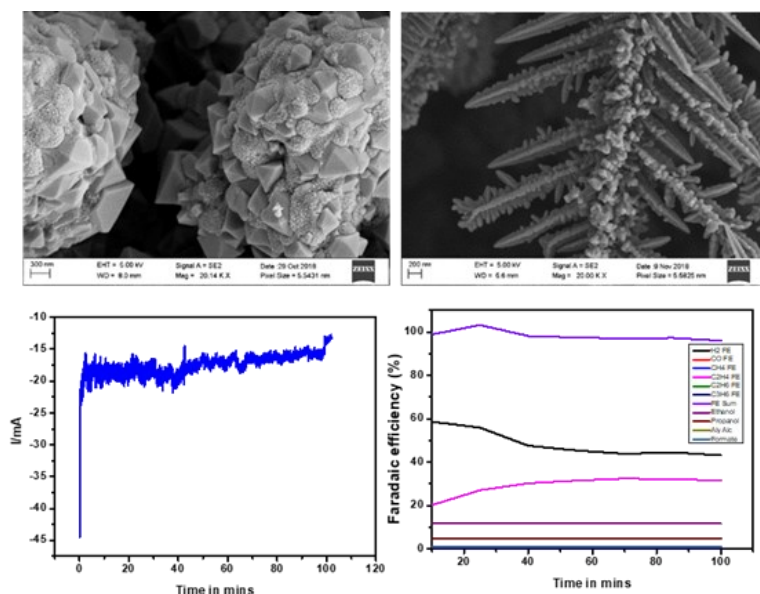


Fig. 6.3: Dendrite like Cu nanostructures derived from Cu₂O as an active catalyst and its electrocatalytic performance.

Dr Divya NAGARAJU

Update on work package 2 Modelling and data informatics

Dr Kuppa Ashoke RAMAN (Research Fellow, NUS), after completing the initial ground work on developing a two dimensional electrochemical reactor, has performed a sensitivity analysis for the same system. The performed Monte Carlo analysis will help in providing insights about the dominant parameters influencing the efficiency of the reactor. In particular, the role of different parameters affecting the system performance at different operating voltages has been investigated. The information on the dominant parameters affecting the reactor at different operating condi-

tions will be used in optimising the reactor design. While these parameters give an overview about the reactor design, a one dimensional model has been implemented to optimise the gas diffusion electrode. The residence profile of the reactants and obtained products along the electrode thickness were modelled. A parametric study on the variation of the catalyst and diffusion layer thickness was investigated. We are currently extending this model to augment the effect of wettability and model liquid products.

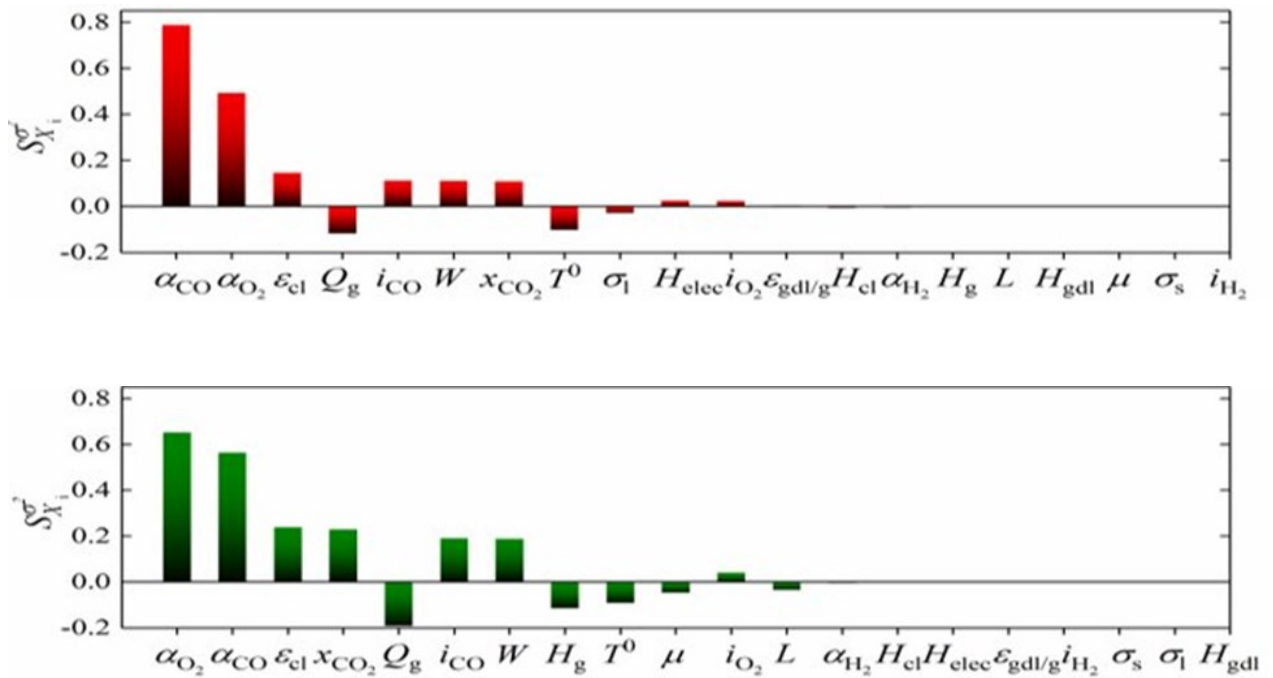


Fig. 6.4: Influence of different operating parameters on the CO₂ conversion efficiency at operating voltage of 3.0 V (top) and 2.3 V (bottom).

Finally, it is well known from literature that the flow field in the gas flow channel influences the performance of a fuel cell. A study on the role of the flow channel geometry on the mass transfer effects is undertaken. A preliminary study was conducted to investigate the effect flow field inside the gas flow channel and diffusion layers for

different channel configurations. For the conditions considered, a uniform distribution of the reactants inside the flow channel and GDL was observed. However, deviations from this uniformity are expected once reaction source terms are implemented in the 3D model.

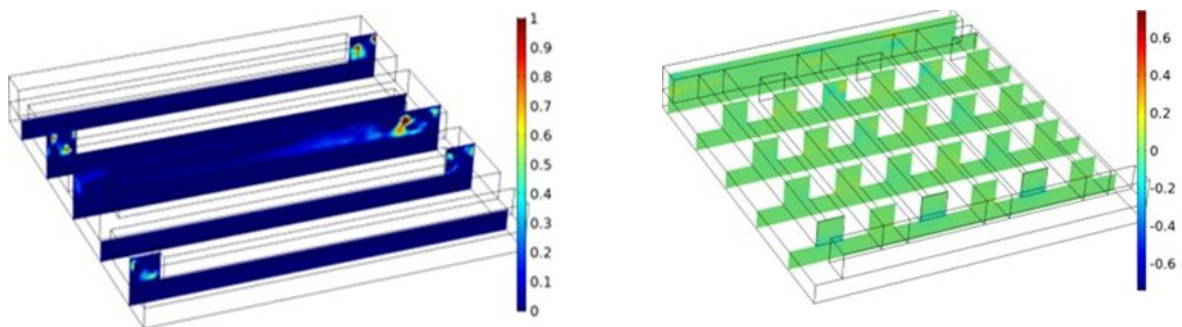


Fig. 6.5: Contour plots of w -velocity component for interdigitated (left) and serpentine (right) flow channel geometries.

Dr Kuppa Ashoke RAMAN

Dr Quang Thang TRINH (Victor) (Research Fellow, NTU) used density functional theory (DFT) calculations to help design catalysts for CO₂ reduction. DFT simulations helped to predict the XPS signal corresponding to the subsurface boron inside the lattice of the copper (Cu) catalyst. These results are great help in the structural characterisation of the synthesised novel catalyst developed for CO₂ reduction. The catalyst samples were also sent to a collaborator at Rutgers University for further depth-profile and angle-dependent XPS analysis.

Besides this, Dr Trinh observed that the electronics properties of Cu (reflected via the projected d-band density of states of Cu) could be significantly modified upon supporting of graphene oxides. This observation could open a new avenue in enhancing the activity and selectivity for Cu catalysts in CO₂ reduction.

Dr Trinh, under the supervision of Dr Matthew SHERBURNE (PI, BEARS) and a collaborator from the CSIR-Indian Institute of Chemical Technology (Prof. John MONDAL) has successfully fabricated the novel material graphene-nanosheet

-supported ultrafine Cu nanoparticles with well-defined sizes, which were encapsulated with thin mesoporous silica (Cu-GO@m-SiO₂). Cu nanoparticles with different particle sizes of 7.8 nm, 13.2 nm and 60 nm have been synthesised via three different routes and were evaluated in a test case – the oxidative coupling of aromatic amines producing biologically and pharmaceutically important imine derivatives. It was shown that the newly developed catalysts effectively promoted the reaction with high selectivity. Prominent size-dependent catalytic activity of various sized Cu nanoparticles in this oxidative coupling was reported. Furthermore, this newly designed sandwich catalyst showed very good tolerance to a diversity of amine substrates and exhibited excellent stability in cyclic tests.

By adopting the DFT calculations for all the elementary reaction steps on different active sites of Cu nanoparticles, results revealed that the step sites play a crucial role in promoting the reactant activation and facilitating the C-N coupling reaction, which correlates nicely to the experimental observation. On terrace Cu(111) sites which dom-

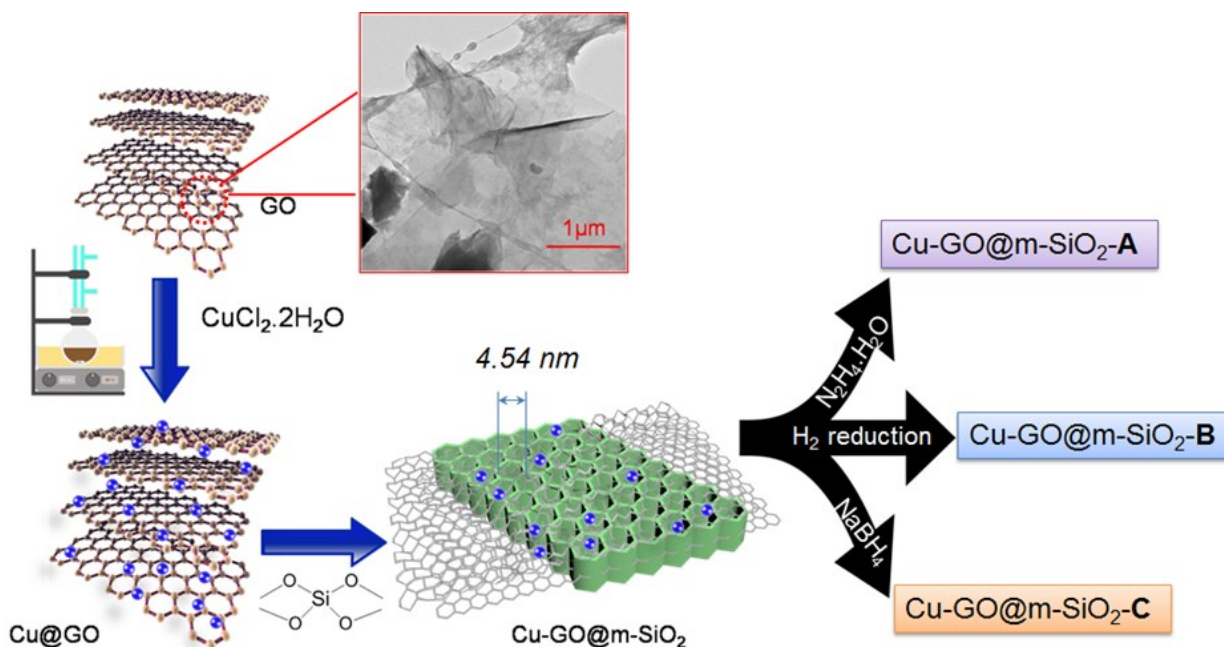
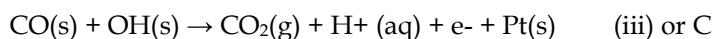
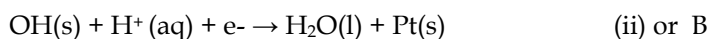
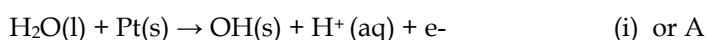


Fig. 6.6: Schematic illustration for the synthesis of novel material graphene-supported Cu nanoparticles encapsulated by mesoporous silica Cu-GO@m-SiO₂.

Dr Quang Thang TRINH (Victor)

inate the large-size of Cu nanoparticles, the activation barriers of the elementary steps during conversion were very high, correlating with its low conversion. However, all those barriers were lower by a magnitude of 15-30% on step sites which were presented in higher density on smaller sized Cu nanoparticles and it explained the higher activity of smaller Cu-GO@m-SiO₂ samples. Insights from DFT simulations may also be able to explain the higher performance of the catalyst under aerobic conditions, with the surface chemisorbed oxygen lowering the barrier to smaller than 0.8 eV, making the reaction feasible at experimental conditions.

Martin MARTIN (Research Scientist, CARES) reports that experimental design is an important aspect of achieving suitable conditions for efficient conversion of CO₂ into other valuable chemicals using electrochemistry. The goal is to maximise the desired products and minimise the energy used. Computational modelling is a suitable approach to solve this optimisation problem. Modelling in electrochemistry requires improvement in terms of accuracy and features, particularly with respect to macrokinetics. At present, an oversimplified model using the Butler-Volmer equation is used almost as a benchmark in electrochemical kinetics, despite requiring many assumptions and data fittings using experimental data. Thus, the Butler-Volmer equation can be said to be outdated in the current climate of advanced computing.



Reaction (i) represents an elementary reaction of *dissociative water oxidation*, whereby a water molecule dissociates into OH(s), OH species on sitting on the Pt(s) surface and H⁺ which is an ion present in the liquid phase. Reaction (i) is an absorption of OH into the surface. Reaction (ii) is the reverse of Reaction (i), where desorption of H(s)

This synthetic strategy thus demonstrated that sandwiched structures with engineering active sites could provide a multipurpose approach to refine catalysts, in efforts to improve the selectivity of industrially valuable catalytic reactions. The paper based on these results has been published in *ACS Applied Materials & Interfaces*. This novel synthesised catalyst has also been sent to colleagues in eCO₂EP to test for CO₂ reduction.

However, it is easy to ignore more accurate models of macrokinetics such as the Marcus theory of electron transfer, which was postulated and developed by a 1992 Nobel Prize winner in chemistry. Marcus theory can be used to help solve pathways (optimise) in CO₂ conversions into products with two or even three carbon atoms. Marcus theory takes thermodynamic reversibility into consideration, and thermodynamics data for all species involved are required. The rate constant, *k*, which is required to calculate the rate of progress of a reaction, is calculated using the modified Arrhenius expression, in which the parameters are obtainable using DFT simulation. Here is a simple example whereby a simple CO oxidation on platinum consisting of three elementary reactions is solved using Marcus theorem.

occurs and an empty site of Pt(s) results. Reaction (iii) occurs when H(s), a surface hydrogen atom and a surface OH atom sit next to each other on Pt(s) surface. Reaction (iii) has slow and fast forward rate constants.

Equation of systems (ordinary differential equations) must be solved:

$$\frac{d\theta_{\text{OH}}}{dt} = k_{f,A}(1 - \theta_{\text{OH}} - \theta_{\text{CO}}) - k_{f,B}(\theta_{\text{OH}}) - Zk_{f,C}(\theta_{\text{OH}}\theta_{\text{CO}})$$

$$\frac{d\theta_{\text{CO}}}{dt} = -Zk_{f,C}(\theta_{\text{OH}}\theta_{\text{CO}})$$

Initial conditions must be given in the model such as site density (Γ) which is 1.32×10^{15} sites per cm^2 , surface coverage of CO (θ_{CO}) is 0.99, surface coverage of OH (θ_{OH}) is 0.0. The voltage is ramped between 0.1 to 0.5 Volts in this model with a sweep rate of 50 mV per second. $k_{f,i}$ is the forward rate constant for reaction i and Z is the number of nearest neighbours on the surface Pt

sites. Z is a factor that is applied to Reaction 3. The Pt available sites (θ_{Pt}) can be calculated using the sites conservation such that

$$\theta_{\text{Pt}} = 1 - \theta_{\text{OH}} - \theta_{\text{CO}}$$

The evolution of surface species Pt(s), CO(s) and OH(s) can be seen in the figures below.

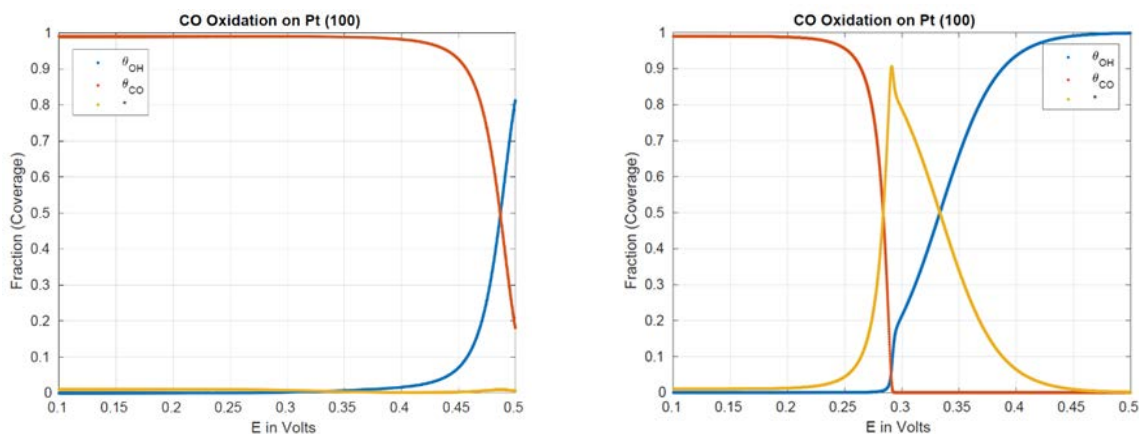


Fig. 6.7: **left** evolution of surface species coverage as a function of applied voltage in the case where a slow CO oxidation reaction occurs. **right** evolution of surface species coverage as a function of applied voltage in the case where a fast CO oxidation reaction occurs.

Martin MARTIN

Update on work package 3

Chemical factory on a table

Dr Souradip MALKHANDI (Research Fellow, NUS) has been working on the development of a table-top reactor for CO₂ electro-reduction. Electrochemical CO₂ reduction is one of the potential green chemical methods to convert CO₂ to valuable precursors for chemical industry such as ethylene and propanol.

The objective of Dr Malkhandi's work is to develop a reactor to convert CO₂ to ethylene electrochemically. The heart of this reactor is a gas diffusion electrodes (GDE) system which reduces CO₂ electrochemically. Usually, GDE is a complex multilayer porous electrode system where electrochemical reactions take place. In a typical GDE, the metrics of performance are current density, selectivity (Faradic efficiency and partial current density), and life time. The state of the art CO₂ to ethylene type GDEs operate around 100 mA/cm² current density with 60-70% faradic effi-

ciency and tens of hours of life time. The initial version of high performance GDE for ethylene, which is developed at CARES by Dr Malkhandi, runs at 300 mA/cm² with above 40% Faradic efficiency, and 5+ hours life time (Figure 6.8a). Besides GDE development, Dr Malkhandi has been working on the design of the reactor and automation system. The first model of reactor design for 10 cm² electrode area has been completed and a 3D printed prototype is under testing (Figure 6.8b). A LabVIEW software based data acquisition and control program for reactor automation has been developed (Figure 6.8c). This software program controls gas flow, current, voltage, temperature, pressure, other system parameters of the reactor. A further extension of GDE life time, and higher faradic efficiency are two major goals of Dr Malkhandi's future work.

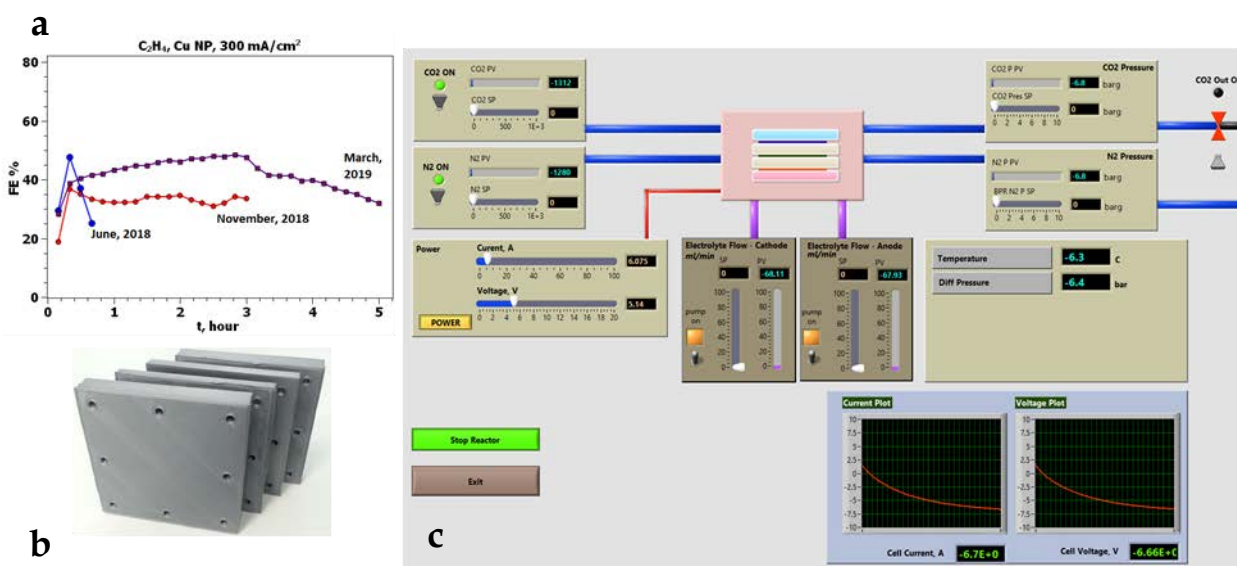


Fig. 6.8: **a** Faradic efficiency vs time plot for ethylene production, the blue curve is the status of GDE at the very beginning of the project, where it worked for 40 minutes, the red curve is showing the improved version of GDE which is stable up to 3 hours, and the purple curve is showing the performance of latest GDE, which is stable for 5 hours **b** 3D printed first prototype of reactor **c** Showing the control panel for reactor automation software system written using the LabVIEW program.

Dr Souradip MALKHANDI

Alexandr KHUDOROZHKOV's (Research Assistant, CARES) main aim is the development of a separation part of a table-top factory to selectively isolate ethylene and 1-propanol from the mixture of all possible CO₂ reduction products. Due to low concentrations of desired products and the complicated structure of the steam-gas mixture (CO₂, H₂, H₂O, C₂H₄, C₃H₇OH, CO, CH₄) a suitable pathway for the successful separation should provide high selectivity to ethylene and propanol and demonstrate high stability with time.

Assuming this fact, several possible ways of development the separation part were developed. It includes either the utilisation of modified zeolites, or metal-organic frameworks (MOFs), or mixed matrix membranes (MMMs). All these materials should provide the molecular sieving and chemisorption separation effects. Analysis of literature and preliminary simulations showed that MOFs based on dioxidobenzenedicarboxylic acid (dobdc) or 4 Å molecular sieves ion exchanged with some d-metals can be suitable for selective separation of desired components from the final mixture. Accurate adjustment of the MOFs' or zeolites' structure can lead to the significant enhancement of selectivity and adsorption capacity of a material. Figure 6.9, adapted from the literature shows the differences in adsorption of C₂H₄ on Co-based MOF with meta- or para-orientation of hydroxyl-groups in dihydroxyterephthalic acid, which forms the framework of MOF. Some of these structures have already been synthesised. Characterisation of samples and conduction of separation experiments would be the next step.

A second possible route of selective separation of ethylene is a chemical loop, which assumes a selective reaction of C₂H₄ with water forming liquid ethanol. Ethanol is then condensed and dehydrated with a formation of ethylene. Via the Aspen simulations it was shown that this method could be used for ethylene separation but more detailed studies are needed.

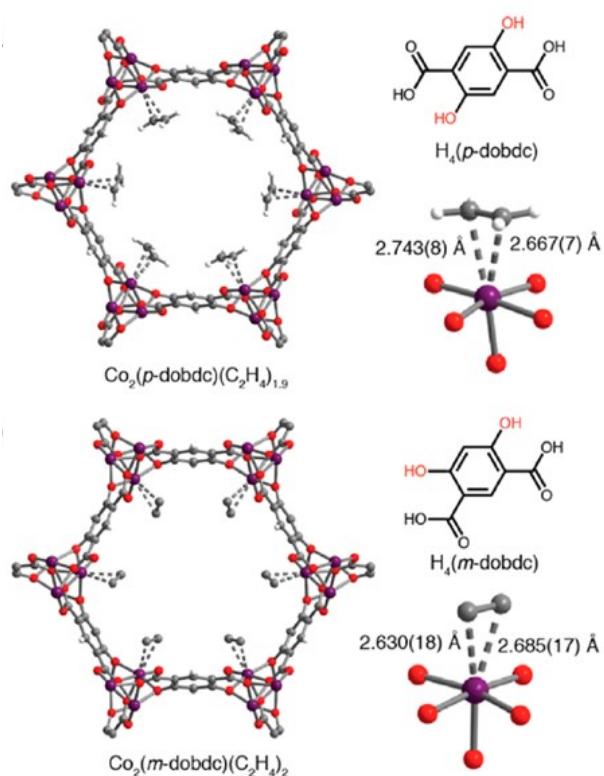


Fig. 6.9: Differences in orientation and bonding of ethylene with a structure of MOF forming ligand (meta- or para-dobdc) (Bachman et al., *Journal of American Chemical Society*, **139**, 2017, 15363-15370).

Alexandr KHUDOROZHKOV

Scientific output

The following are the CREATE-acknowledged publications generated by eCO₂EP during the reporting period, excluding that already featured in the Scientific Highlights section on page 13.

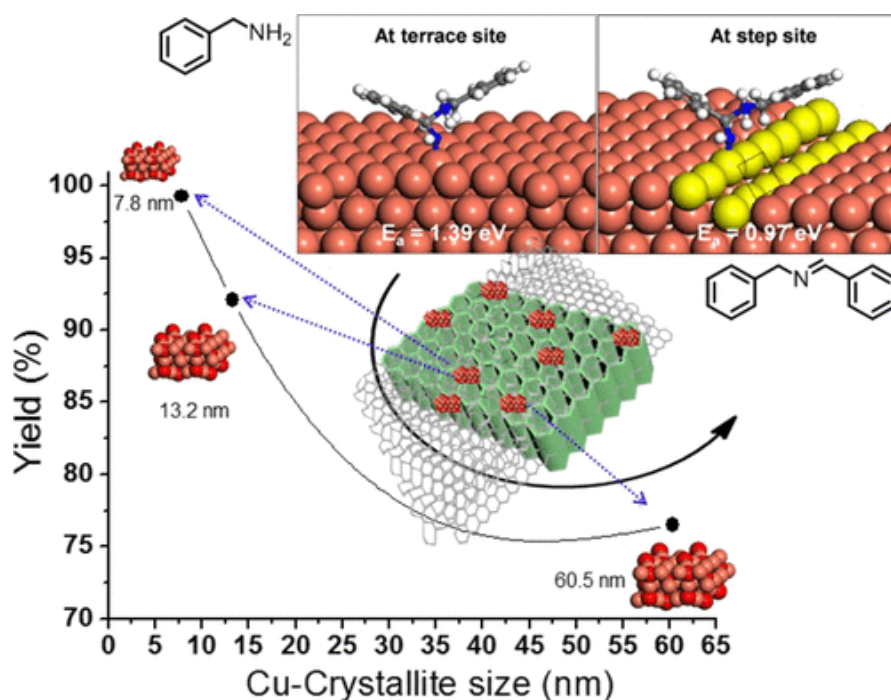
Interface Engineering of Graphene-Supported Cu Nanoparticles Encapsulated by Mesoporous Silica for Size-Dependent Catalytic Oxidative Coupling of Aromatic Amines

Chitra Sarkar, Saikiran Pendem, Abhijit Shrotri, Duy Quang Dao, Phuong Pham Thi Mai, Tue Nguyen Ngoc, Dhanunjaya Rao Chandaka, Tumula Venkateshwar Rao, Quang Thang Trinh, Matthew Sherburne and John Mondal, *ACS Applied Materials & Interfaces*

DOI: 10.1021/acsami.8b18675

Abstract: In this study, graphene nanosheet-supported ultrafine Cu nanoparticles (NPs) encapsulated with thin mesoporous silica (Cu-GO@m-SiO₂) materials are fabricated with particle sizes ranging from 60 to 7.8 nm and are systematically investigated for the oxidative coupling of amines to produce biologically and pharmaceutically important imine derivatives. Catalytic activity remarkably increased from 76.5% conversion of benzyl amine for 60 nm NPs to 99.3% conversion and exclusive selectivity of *N*-benzylidene-1-phenylmethanamine for 7.8 nm NPs. The superior catalytic performance along

with the outstanding catalyst stability of newly designed catalysts are attributed to the easy diffusion of organic molecules through the porous channel of mesoporous SiO₂ layers, which not only restricts the restacking of the graphene nanosheets but also prevents the sintering and leaching of metal NPs to an extreme extent through the nanoconfinement effect. Density functional theory calculations were performed to shed light on the reaction mechanism and to give insight into the trend of catalytic activity observed. The computed activation barriers of all elementary steps are very high on terrace Cu(111) sites, which dominate the large-sized Cu NPs, but are significantly lower on step sites, which are presented in higher density on smaller-sized Cu NPs and could explain the higher activity of smaller Cu-GO@m-SiO₂ samples. In particular, the activation barrier for the elementary coupling reaction is reduced from 139 kJ/mol on flat terrace Cu(111) sites to the feasible value of 94 kJ/mol at step sites, demonstrating the crucial role of the step site in facilitating the formation of secondary imine products.



Other activities and achievements

Dr Divya NAGARAJU (Research Fellow, NTU) attended the 8th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications in Innsbruck, Austria from 4-8 February 2019. She presented a poster with the title 'Functional nanomaterials for electrochemical CO₂ reduction investigated using PTR-TOF MS for real time product identification' (co-authors Lily Mandal, Peter Lobaccaro, Alexei Lapkin, Joel Ager and T Venkatesan).

eCO₂EP held an open workshop and a closed one-year progress meeting in Singapore, in March 2019, led by Prof. Alexei LAPKIN (CARES) and Prof. Joel AGER (BEARS). Researchers presented tutorial-style presentations on separation, counter chambers, proton-transfer-reaction mass spectrometry (PTRMS) and flame synthesis.



Dr Quang Thang TRINH (Victor) presents his work at the eCO₂EP meeting in March.

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DOI: 10.1038/s41467-018-06269-z

OPEN

Hydrogen spillover through Matryoshka-type (ZIFs@)_{n-1}ZIFs nanocubes

Guowu Zhan^{1,2} & Hua Chun Zeng^{1,2}

Hydrogen spillover phenomenon
highly disputed in hydrogen
metal...

PUBLICATIONS

Energy 150 (2018) 1039–1057

Contents lists available at ScienceDirect

Energy

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environmental power dispatch with
all hydro power

ian^a, B.Y. Qu^b, Gehan A.J. Amaratunga^c

g Technological University, Singapore
yuan University of Technology, China

Selective Electrochemical H₂O₂ Two-Electron Oxygen Electro

Yuanyuan Jiang, Pengjuan Ni, Chuanxia Che,
Biao Kong, Adrian Fisher, and Xin Wang*

Direct electrochemical production of hydrogen peroxide (H₂O₂)
two-electron oxygen electrochemistry, for example, the oxygen re
in fuel cells or water oxidation in water electrolyzers, could provi
attractive alternative to locally produce this chemical on demand
efficiency of these processes depends greatly
effective catalysts with

ALL C4T PUBLICATIONS WITH CREATE ACKNOWLEDGEMENT

The following list includes all the C4T publications from the beginning of Phase 2 (November 2018). For a full record of Phase 1 publications (April 2013 – October 2018) please visit our Publications page on the CARES website: www.cares.cam.ac.uk/publications/.

C4T joint IRP publications

IRP1 and IRP3

- Kan, Xiang, Xiaoping Chen, Ye Shen, Alexei Lapkin, Markus Kraft, and Chi-Hwa Wang. 2019. "Box-Behnken Design Based CO₂ Co-Gasification of Horticultural Waste and Sewage Sludge with Addition of Ash from Waste as Catalyst." *Applied Energy* 242 (May): 1549–61. <https://doi.org/10.1016/j.apenergy.2019.03.176>.

IRP3 and IRP JPS

- Chhabra, Pulkit, Sebastian Mosbach, Iftekhar A. Karimi, and Markus Kraft. 2019. "Practically Useful Models for Kinetics of Biodiesel Production." *ACS Sustainable Chemistry & Engineering* 7 (5): 4983–92. <https://doi.org/10.1021/acssuschemeng.8b05636>.

C4T IRP1: Sustainable reaction engineering

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- Rosli, Nur Farhanah, Michaela Fojtů, Adrian C. Fisher, and Martin Pumera. 2019. "Graphene Oxide Nanoplatelets Potentiate Anticancer Effect of Cisplatin in Human Lung Cancer Cells." *Langmuir* 35 (8): 3176–82. <https://doi.org/10.1021/acs.langmuir.8b03086>.
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C4T IRP3: Combustion for cleaner fuels and better catalysts

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IRP4 (Better, cleaner heat usage) and IRP BB (Pathways to industrial decarbonisation) are new projects in Phase 2, so there are no publications from these IRPs at the present time.



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