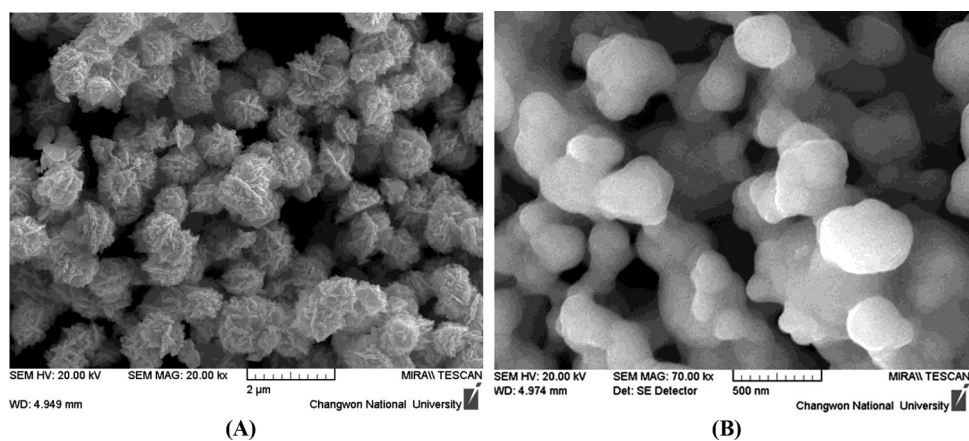# CAMBRIDGE **CARES**

Biannual Research Report

April - September 2020

CAMBRIDGE **CARES**

CAMBRIDGE CENTRE
FOR ADVANCED RESEARCH AND
EDUCATION IN SINGAPORE LTD

Cover image

SEM images of silver nanoparticle substrate: (A) 2 µm scale and (B) 500 nm scale.

Image by Dr Duy Quang Dao, colleague of Dr Victor Trinh Quang Thang (Research Fellow, eCO2EP). Used with permission from ACS Publications. See more on pages 104 and 110.

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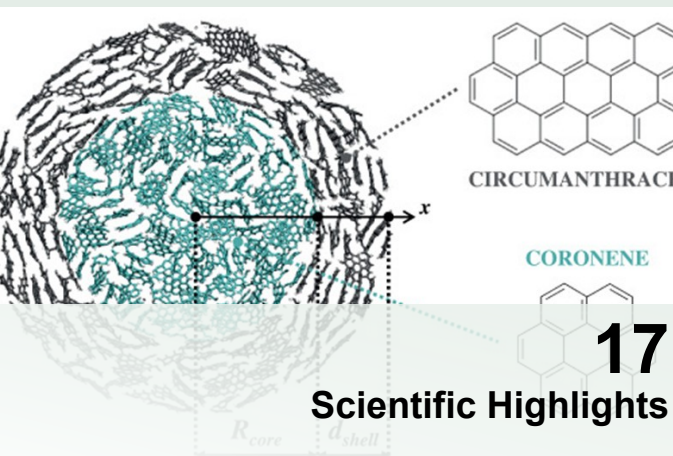
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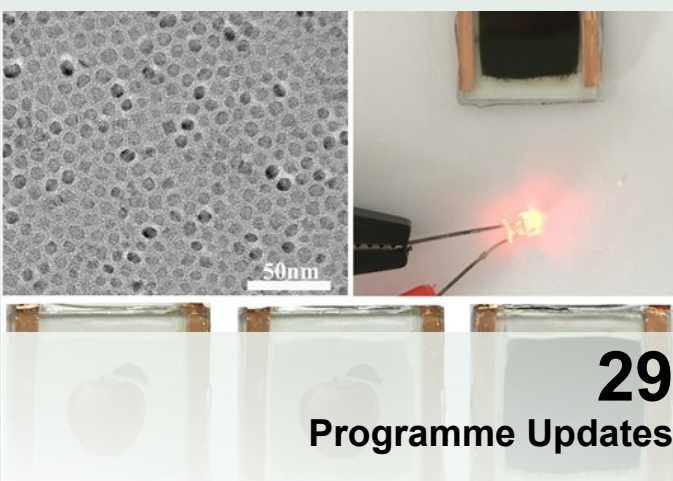
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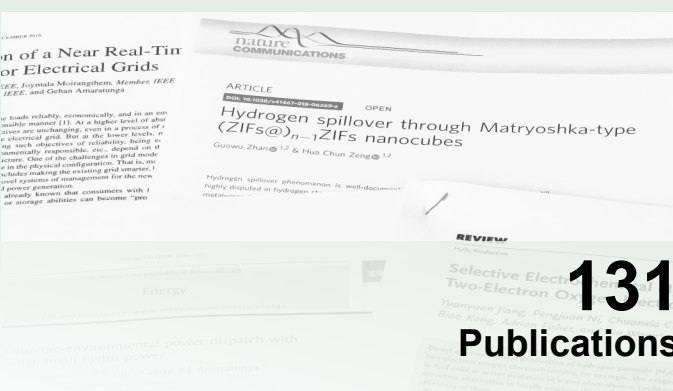
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FOREWORD

I am very pleased to present the 13th Biannual Research Report of the Cambridge Centre for Advanced Research and Education in Singapore (Cambridge CARES). While this year has been like no other in CARES' history, I am proud of the way that our researchers have continued to work hard despite their changed circumstances. Our experimental work has slowed with restricted lab access in Singapore and Cambridge, but I am encouraged to see a number of new publications reported over the past few months, as well as the commencement of new research projects.

MID-TERM REVIEW

The C4T Mid-Term Review took place in June and was a wonderful opportunity to catch up with our Scientific Advisory Committee and share our recent work. The shift to a virtual meeting made scheduling over time zones more difficult, but gave us the chance to try new ways of demonstrating our research, like pre-recorded presentations and virtual poster sessions.

NEW INTRA-CREATE PROJECT

Our latest Intra-CREATE project will also commence on 1st October. *Consumer Energy Usage Data in Smart City Development* (CEUS) is hosted by CARES and led by Dr Franziska Sielker (University of Cambridge) and Dr VSK Murthy Balijepalli (Singapore-ETH Centre). The CEUS project aims to develop a data-driven platform that allows consumers to analyse their energy usage information and make better-informed decisions. The project will also allow for integration of real-time data into city information modelling by linking up with the J-Park Simulator.

CLIC

The *Centre for Lifelong Learning and Individualised Cognition* (CLIC) will be launched on 1st October. CLIC is supported by Singapore's National Research Foundation and is run by Cambridge University and NTU. CLIC takes CARES into new fields of study and will focus on the neuroscience of learning. We look forward to welcoming the Cambridge researchers to Singapore when this travel is possible again.

COOLING SINGAPORE

CARES is pleased to join the Cooling Singapore 2.0 programme, hosted by the Singapore-ETH Centre and starting in late 2020. We will be using our parallel world simulator to better analyse different cooling scenarios as climate change increases urban heating.

VISITING SCIENTISTS

By the beginning of 2020, we had several Visiting Scientists lined up to visit us in Singapore and share their expertise on particulate modelling, biomass conversion and sustainable chemistry. Unfortunately, we have had to postpone their visits but we look forward to welcoming them when travel to Singapore resumes.

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
September 2020

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 CO_2 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.

The second large programme administered by CARES is eCO$_2$EP. 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
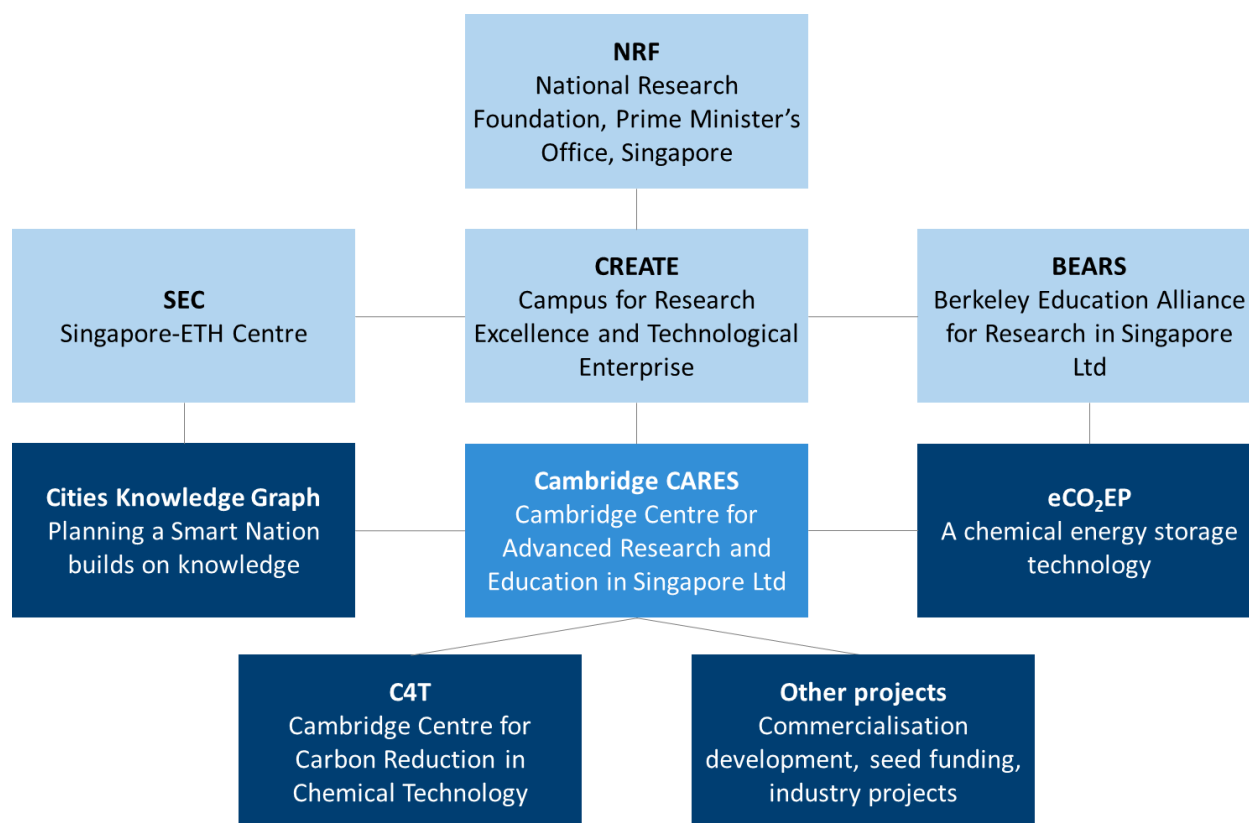
carbon dioxide emitted as part of the industrial process into compounds that are useful in the chemical industry supply chain. This programme is funded by an Intra-CREATE large grant.

As of 1st April 2020, CARES has been awarded a further Intra-CREATE large grant for Cities Knowledge Graph, which brings together researchers from University of Cambridge and ETH Zürich to harness rapidly growing and diversifying data streams to improve the planning and design of cities. Cities Knowledge Graph will do this by developing an innovative digital platform designed to combine data and share knowledge about cities, and to inject new precision and responsiveness to static instruments of planning, such as the city master-plan.

As well as these large Intra-CREATE grants, CARES has several smaller projects ongoing. There is one smaller, seed-funded Intra-CREATE project between CARES and National University of Singapore, and three further projects that involve industry and/or commercial funding. Details and updates for these smaller projects can be found on page 121.

In addition, CARES will start several new projects in October 2020. Details of these can be found in the Foreword.

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.

NRF
National Research Foundation, Prime Minister's Office, Singapore

SEC
Singapore-ETH Centre

CREATE
Campus for Research Excellence and Technological Enterprise

BEARS
Berkeley Education Alliance for Research in Singapore Ltd

Cities Knowledge Graph
Planning a Smart Nation builds on knowledge

Cambridge CARES
Cambridge Centre for Advanced Research and Education in Singapore Ltd

eCO₂EP
A chemical energy storage technology

C4T
Cambridge Centre for Carbon Reduction in Chemical Technology

Other projects
Commercialisation development, seed funding, industry projects

HIGHLIGHTS

OUTSTANDING WORK FROM THE LAST SIX MONTHS OF CAMBRIDGE CARES RESEARCH

FOCUS ON

IMPACT

Gas diffusion electrodes for industrial CO$_2$ utilisation
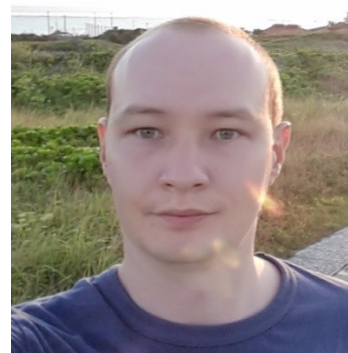
Dr Mikhail KOVALEV, Research Fellow, eCO$_2$EP

In the modern world, energy production plays a vital role in driving progress and improving the quality of life. To date, the primary source of energy is still the burning of organic fossil fuels that produce enormous amounts of the greenhouse gas carbon dioxide. The increased concentration of CO$_2$ is leading to the planet's rapid climate changes. Before the industrial revolution, there was a balance between CO$_2$ produced and that consumed by flora. However, everything changed as the human population started to make more CO$_2$ than the planet can digest. According to NASA's website, the level of carbon dioxide increased by 47% compared to preindustrial levels found in 1850.
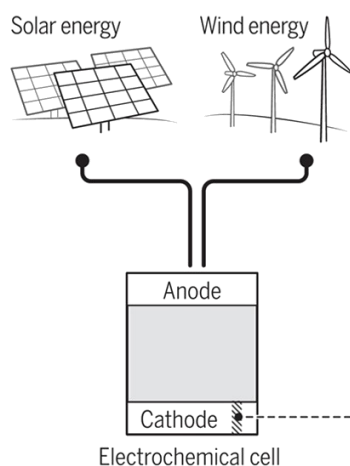
Recently, to mitigate greenhouse gas production, a lot of effort has gone into renewable energy sources such as solar, wind, hydropower, etc. But further technological progress and improvement of quality of life require more energy, so it is not possible to fully substitute fossil fuels. A viable alternative, in this case, is to help the planet to contain an excess of CO$_2$ by capturing it and converting it into useful chemicals, as plants have done for millions of years. Is there any industrial process that can close the CO$_2$ cycle to support our planet?

Here in Cambridge CARES, we are working on electrochemical conversion of CO$_2$ into hydrocarbons such as methane and ethylene. The chemicals can be reused as fuel or utilised by the chemical industry to produce high-performance materials that are heavily used in our everyday lives. The CO$_2$ reduction system consists of a few essential elements where conversion of CO$_2$ into hydrocarbons happens at the electrochemical cell's catalyst. The catalyst itself is deposited on the porous conductive cathode that allows it to work at the interface of three phases: gas (CO$_2$), electrolyte (ion transfer liquid) and solid (the catalyst itself). The types of cathodes which allow the combination of the three phases are called gas diffusion electrodes (GDE).

Dr Mikhail Kovalev received his doctoral degree in 2009 in the Boreskov Institute of Catalysis, Russia with the specialty Physical Chemistry. After receiving his PhD he worked in Samsung Electronics, South Korea from 2010 to 2017. He then came to Singapore and worked in A*STAR before joining the CARES eCO$_2$EP project in April 2020.

OH⁻ (to anode)

A stable and efficient system
Collocation of the catalyst layer and high concentrations of CO_2 and OH^- in a thin 25-nm layer lead to improvements in the conversion efficiency and selectivity for ethylene production. The use of base-stable PTFE for the porous gas transport layer enables continuous operation for 100 hours.

25 nm

Gas diffusion electrode
1 Graphite
2 Carbon nanoparticles
3 Copper nanoparticles
4 Gas-porous PTFE

CO_2 **Ethylene**

Solar energy Wind energy

Anode

Cathode

Electrochemical cell

An example of a gas diffusion electrode.

Ager, Joel W., and Alexei A. Lapkin. 2018. 'Chemical Storage of Renewable Energy'. Science 360 (6390): 707–8. https://doi.org/10.1126/science.aat7918.

V. Altounian/Science

The advantage of GDEs is their ability to work with CO_2 flow and electrolyte simultaneously while preventing the mixing of gas and liquid phases, which makes the product separation process more straightforward. At the same time, the GDE itself has a complicated multilayer structure that needs to comply with experimental conditions. These layers are:

- a conductive current collector layer that supplies electrons to reduce CO_2;

- a catalyst layer where CO_2 reduction happens;

- a porous hydrophobic layer that prevents the electrolyte from flooding into the gas phase while giving access for CO_2 and electrolyte to catalyst;

- a binder layer that sticks all the functional layers together.
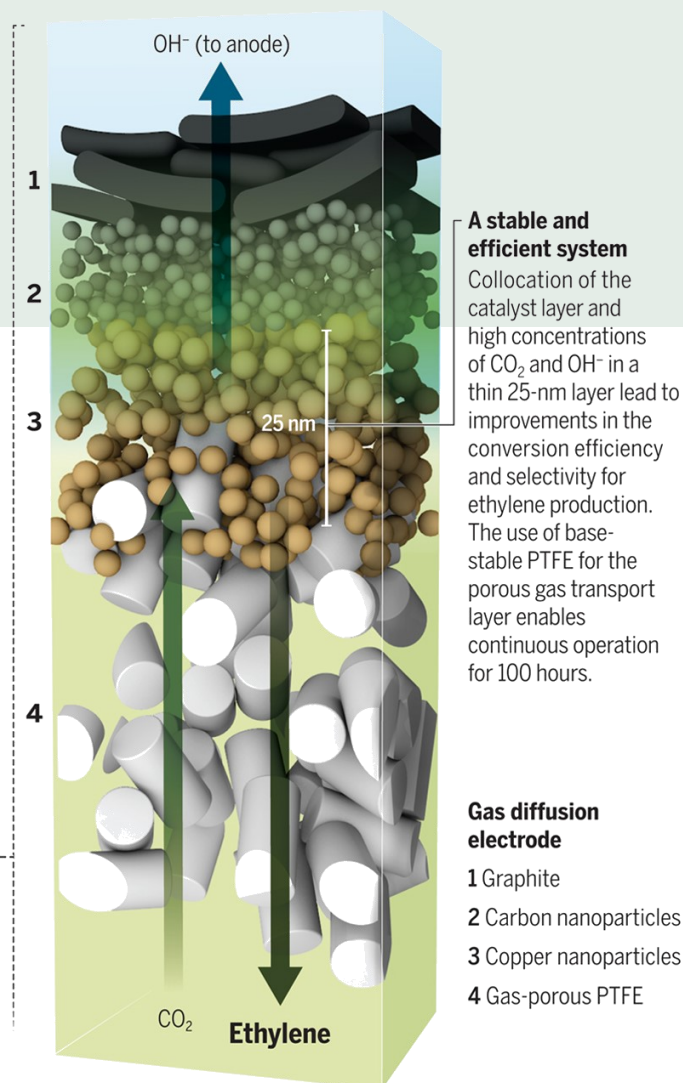
In summary, by tuning parameters of each layer in GDE it is possible to adjust preferable product output. The polymer industry might require ethylene for the production of polyethylene. Carbon monoxide can be used further in the mixture with hydrogen to form synthesis gas and used to synthesise gasoline. New GDEs should be capable of working for longer and producing valuable chemicals with high yield. Therefore, the development and research of new GDEs are some of the most prioritised tasks in the field of carbon dioxide reduction systems.

Reference:

NASA website: https://climate.nasa.gov/vital-signs/carbon-dioxide/ (Accessed 30 Sep 2020)

FOCUS ON
FUNDAMENTAL SCIENCE

A Middle Way: Physical + chemical pathways to soot formation

Dr Jacob MARTIN, Research Fellow, C4T IRP3

A middle way can refer to many things. In common usage it refers to a compromise between two positions. In philosophy or religion, it can refer to a rejection of extremes as exemplified by Aristotle's golden mean that "every virtue is a mean between two extremes, each of which is a vice". In logic it can refer to a fallacy—halfway between a lie and a truth is still a lie and therefore some care is required in proposing such compromising positions. In science it has been used for a variety of justifiable and unjustifiable positions, one famous example being the middle way between physical scales and another being a position we recently put forward for the formation of the pollutant soot.

In the influential paper "The middle way" published in the Proceedings of the National Academy of Sciences of the USA in 2000, Laughlin et al. discussed the challenge in probing the scale between the atomic and macroscopic dimensions. In this mesoscopic region significant gaps exist in our understanding of how atoms and molecules interact, organise and form complex structures. This intermediate scale is too large to be measured by analytical chemical approaches and too small to be approached from the macroscale. Examples include protein folding, high temperature superconductors and disordered or topologically frustrated materials.

Our recent study on the formation of the pollutant soot illustrates the challenges probing the mesoscopic scale nicely. Figure 1 shows a schematic of the transformation of fuel molecules into the pollutant soot. Only in the last five years have experimental techniques allowed for the aromatic soot precursor molecules as well as the earliest nanoparticles to be directly imaged. Mass spectrometry has also allowed for the mass of the clustering molecules to be measured during soot formation. However, the mechanism by which these molecules cluster continues to baffle combustion scientists. The prize sought is the ability to understand and potentially halt the emission of these toxic pollutants from internal combustion engines that damage almost every organ in our bodies as well as contribute to climate change.

Jacob is a PhD student in the Cambridge Computational Modelling group and a member of Churchill College. He completed a Bachelor of Science with First Class Honours in Chemistry and Physics followed by Masters in Chemistry at the University of Auckland (New Zealand). This included research in the areas of ultrafast spectroscopy, Raman spectroscopy, Bayesian data analysis, computational chemistry and microfluidics. Jacob has strong interests in renewable energy, pollution reduction and carbon nanomaterials. He uses physical models and simulations to describe the chemical world and is developing instruments to measure chemical properties. For his PhD Jacob studied the formation of soot in engines using molecular dynamics and quantum chemistry to look at gas-soot interactions and self-assembly processes within soot/carbon materials.
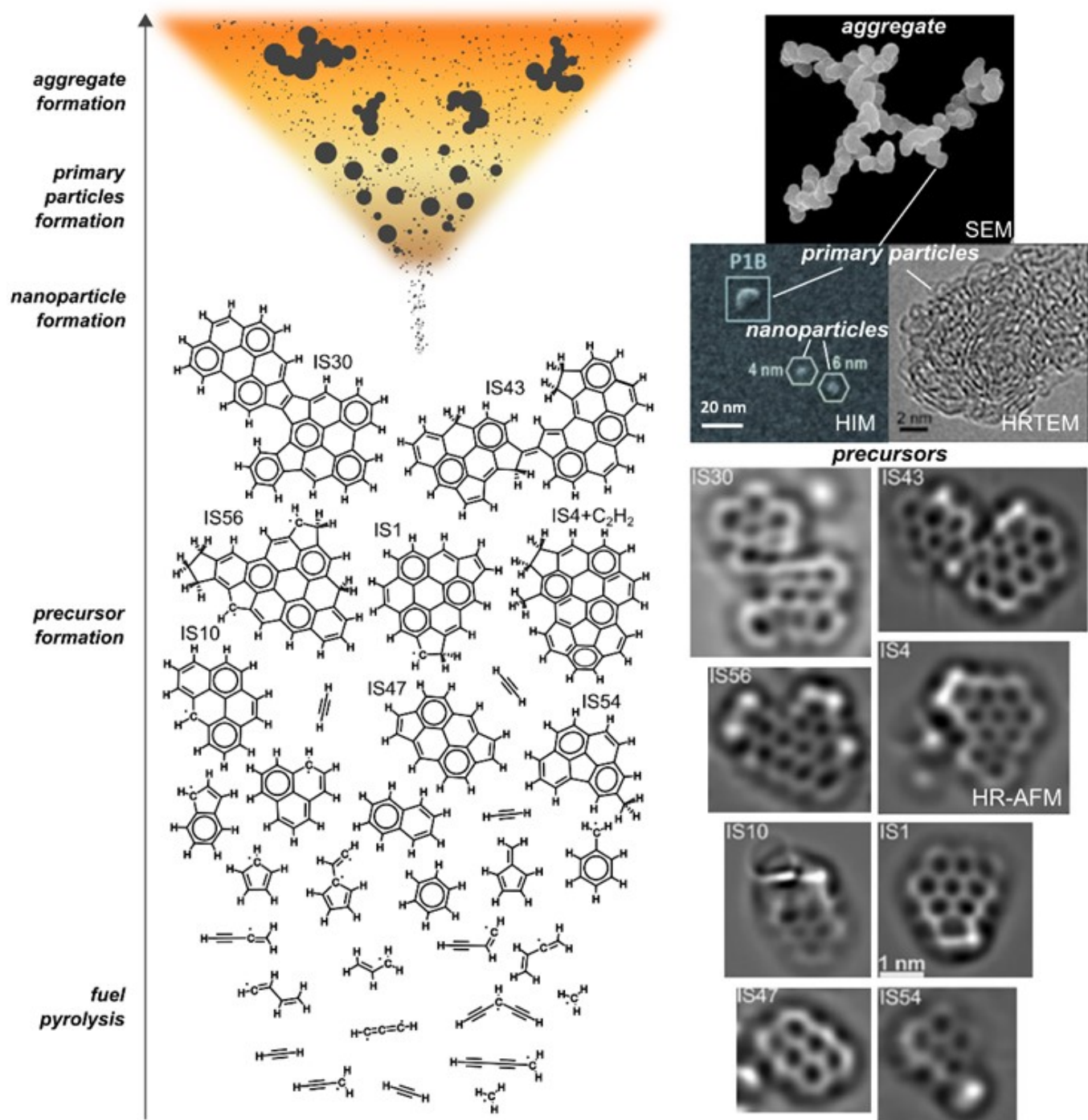
Fig. 1: Schematic for the transformation of fuel into soot inside a flame with insets showing the experimental results from which the schematic is derived. High resolution atomic force microscopy (HRAFM)from Commodo et al. 2019, Helium ion microscopy (HIM) from Schnek et al. 2013, high resolution transmission electron microscopy (HRTEM) from Martin et al. 2018 and scanning electron microscopy (SEM) from Orion carbons.

Our modelling efforts also struggle to traverse the molecule to nanoparticle transition in soot formation. There are two main classes of models that have been proposed for soot formation. The first is physical nucleation, where aromatic molecules grow until the intermolecular interactions between the molecules allows them to stick together and condense. The second is chemical inception, where bonds form between the molecular systems. Only recently have accurate computational approaches been developed to explore these suggestions.

Concerning physical nucleation, Prof. Markus Kraft's group worked with the physical chemist Prof. Alston Misquitta (Queen Mary University) in the 2010s to accurately compute the intermolecular interactions between aromatic species (using a symmetry adapted perturbation with a hybrid density functional approach). From these results it was clear that the clustering species seen in the flame are far too small to possess the signif-

icant intermolecular energies required for physical nucleation mechanism. For my PhD, I explored electrical enhancements to physical nucleation that arise from curved aromatic species that possess a strong electric polarisation. While this electrical effect may help explain the electrical control of soot formation, this alone cannot justify a nucleation mechanism either.

Concerning chemical inception, we recently undertook a systematic study of the bonds that could form between reactive aromatic soot precursors with Prof. Xiaoqing You's group at Tsinghua University (made possible by the CARES programme). This was only possible due to the direct imaging of the reactive aromatics in 2019 (see Figure 1) and the recent advances in density functional computational techniques optimised for radicals (the meta hybrid GGA density functional method M06-2X). Figure 2 shows the systematic comparison that was possible with such an approach for small aromatic molecules. The

	aryl σ-radical		localised π-radical		delocal. π-radical	diradicaloid		rim-based pentagon	cPAH	low aromaticity		Classes
	A1)	A2)	B1)	B2)	C)	D1)	D2)	E)	F1)	F2)	F3)	Structures
aromatic aryl-linked hydrocarbons (AALH)	-130.4	-125.3	-97.3	-91.0	-73.6	-63.7	-78.2	-53.5	-41.3	-38.3	-36.2	A1)
		-120.8	-92.6	-86.8	-69.0	-57.6	-73.3	-49.8	-38.4	-33.7	-33.8	A2)
aromatic rim-linked hydrocarbons (ARLH)			-61.9	-34.0	-39.9	-32.2	-43.8	-24.5				B1)
				-50.9	-33.4	-28.6	-14.8					B2)
aromatic multicentre-linked hydroc. (AMLH)					-17.0	-12.1	-23.6					C)
aromatic zigzag-linked hydrocarbons (AZLH)						-29.6						D1)
							-16.5					D2)

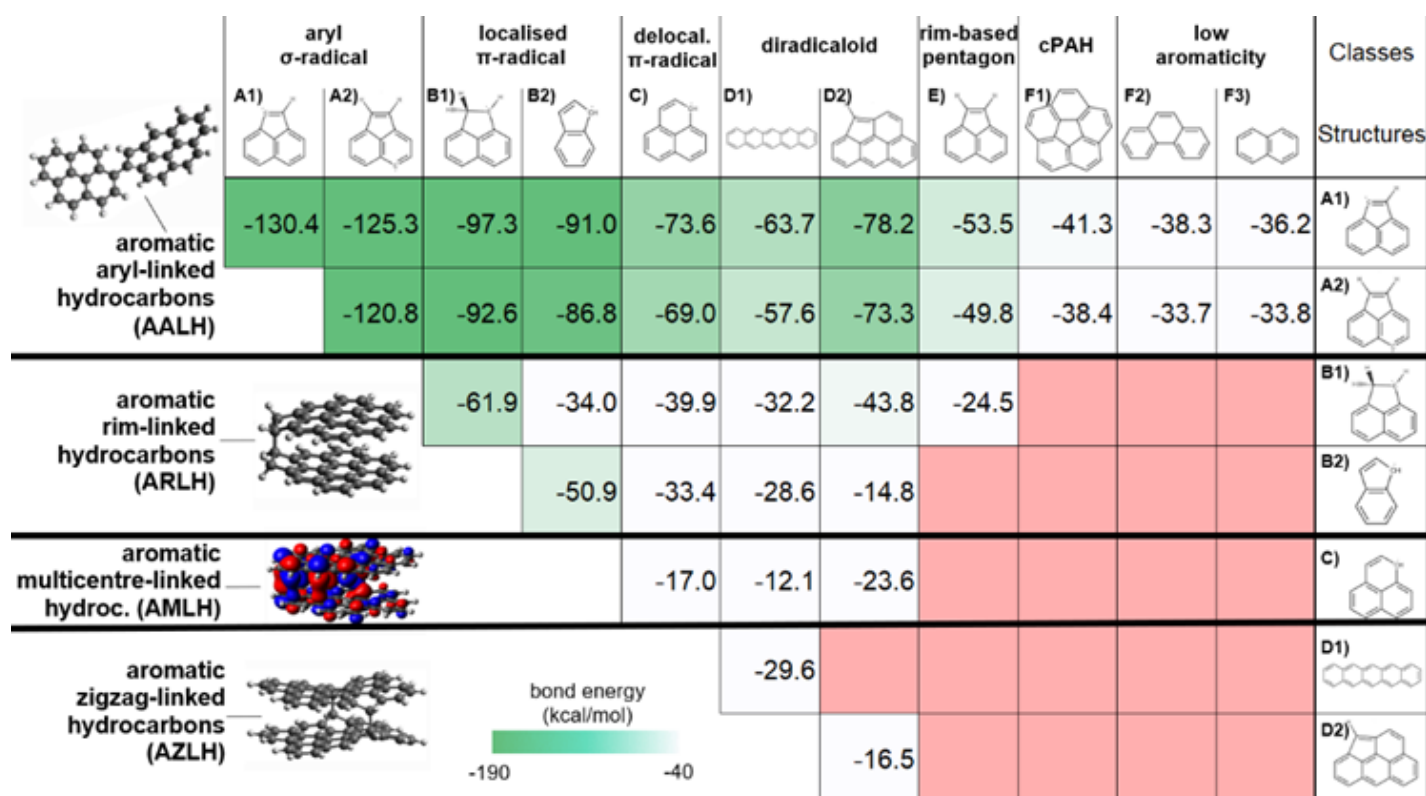bond energy (kcal/mol)
-190 — -40

Fig. 2: Bond energy between various reactive aromatic soot precursors. Green indicates bonds that have enough thermal stability to be considered as important in flames.
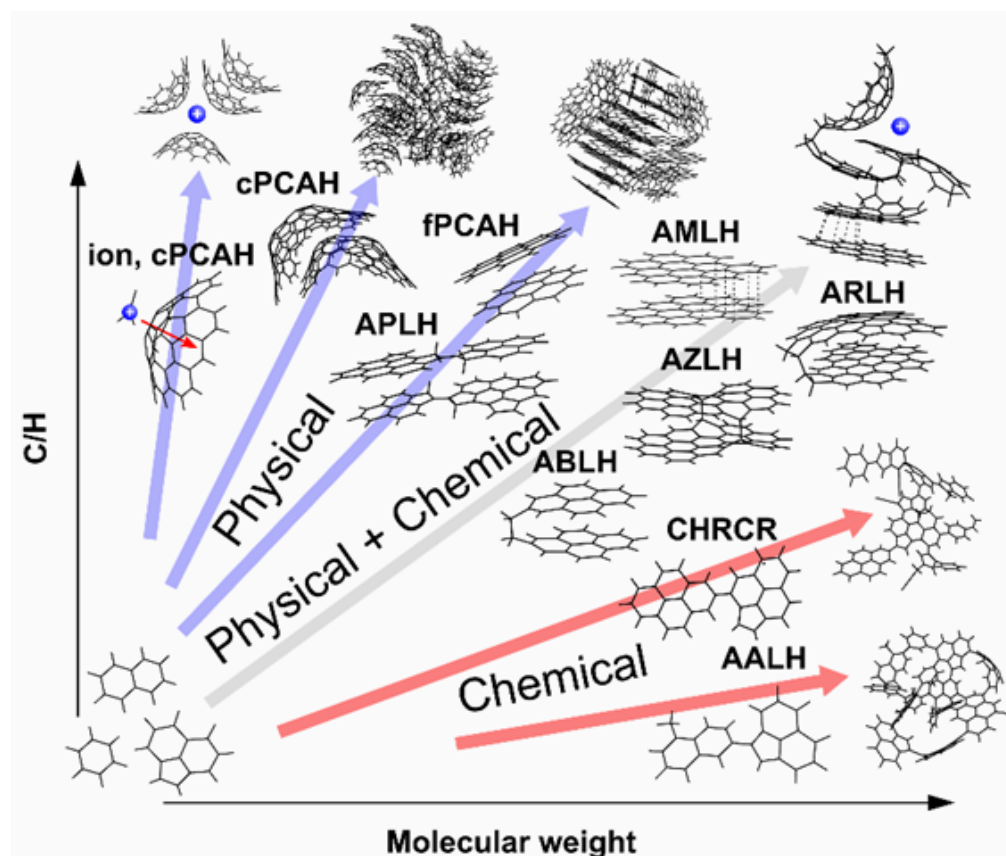
Fig. 3: Pressure distribution along (a) circular and (b) oblique tubes at 0.0262 kg/s.

green grid squares correspond with thermally stable species. Mr Angiras Menon was recently able to compute the rate at which each of these crosslinks forms and compared them with the speed of soot formation. We found that for these small species none of the crosslinks formed sufficiently fast enough to explain the rapid clustering of molecules into soot nanoparticles.

These detailed studies left us with the uncomfortable conclusion that the two main routes proposed for soot formation were unable to describe it. However, something else did catch our attention—crosslinks that allowed the molecules to both bond and stack (see Figure 2's **B)**, **C)** and **D)** sites). This opened up another possibility that both physical and chemical mechanisms could cooperatively contribute to soot formation. Upon exploring these possibilities, we found that π-radicals on five-membered rings, site **B)**, formed highly localised states that did not become deactivated as the molecule grew in size, unlike their hexagonal ring equivalent, thereby remaining

highly reactive. This allowed for an additive contribution between the physical interactions and the chemical bond only in these so-called aromatic rim-linked hydrocarbons (ARLH). Figure 3 shows the various mechanisms placed on a C/H versus molecular weight schematic to show the middle way suggested.

As mentioned at the beginning of this article, claims to middle ways are poor arguments unless they can be justified. Currently, we have shown that the addition of physical interactions and chemical bonding considerably increase the thermodynamic stability of aromatic rim-linked hydrocarbons. However, we have yet to show that such species can explain the rapid formation of soot in the flame. This requires the collision efficiency between these species and the concentration of the localised π-radicals on five-membered rings to be determined. Experiments are underway in the community to probe such species and close the gap between the micro- and macroscale of soot formation.

Automating chemical synthesis using machine learning and programmable chemical handling equipment

Dr Simon SUNG, Research Fellow, PIPS

Dr Mohammed JERAAL, Research Fellow, PIPS

The development of active pharmaceutical or agrochemical ingredients involving many scientists and engineers from various disciplines is a time-consuming and expensive process. A recent study from 2020 reported that it often takes several years to bring an active chemical ingredient from when it is discovered to being publicly available, and on average costs approximately US$1.3 billion.[1] A notable time-consuming part of the development process is in optimising a method for preparing and purifying the active chemical in a large-scale chemical manufacturing plant. Furthermore, this manufacturing process must satisfy several objectives such as yield, cost, and health and environmental impact. It is important to note that optimising the purification is as significant as the chemical preparation to the whole process because it will similarly affect the desired objectives, and also subsequent chemical processes, where any negative aspects often become compounded downstream.

A significant reason why the optimisation of chemical processes is time-consuming is the millions of possible combinations of chemicals, temperatures and pressures (reaction parameters) that can be used to produce a given desired chemical, where each have their own unique yield, cost, and health and environmental impact. The reaction parameters are typically chosen through scientific intuition by R&D scientists, as well as through statistical methods. However, the risk of bias by scientists to design methods based on their experience, and the inefficient, and data intensive statistical methods commonly used have negative time and cost implications. To overcome these issues, the work conducted at Cambridge CARES as part of the Pharma Innovation Programme Singapore (PIPS), in collaboration with GlaxoSmithKline, Pfizer, Merck Sharp & Dohme (MSD), and Syngenta, will utilise an artificial intelligence method called machine learning (ML) to rapidly identify sustainable and

Simon received his MSci degree in chemistry from Imperial College London in 2011 where he performed R&D on new multi-metallic MRI bioimaging agents under the supervision of Dr James Wilton-Ely. As part of his degree he spent one year in industry at the Home Office Scientific Development Branch. In 2015, he obtained his PhD degree at Imperial College London under the supervision of Dr Rob Davies (IC), Prof. Chris Braddock (IC), Prof. Alan Armstrong (IC), Dr David Sale (Syngenta), and Dr Colin Brennan (Syngenta) as part of the Pharmacat Consortium, where he investigated the mechanism of the modified Ullmann reaction. He then moved to the National University of Singapore, spending four years as a Research Fellow in Prof. Rowan Young's laboratory developing new complexes for unique bond activation chemistry and catalysis.
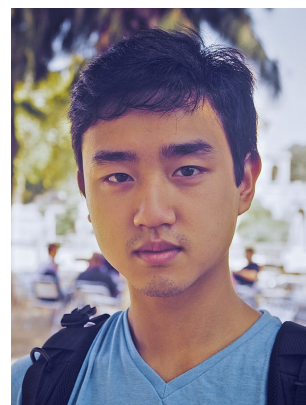
high yielding parameters in fewer experiments for a desired chemical preparation and purification simultaneously.

The work involves fully automated optimisation that combines programmable chemical handling equipment, analytical tools, and ML (Figure 1), where the ML algorithm is taught how certain reaction parameters affect the objectives in real-time. Firstly, using an in-house developed computer application that oversees all operations, the ML algorithm suggests a set of reaction parameters, and initiates the chemical handling robots and reactors to start a process. After a pre-defined amount of time, automatic analyses and data processing are performed to determine the outcome. This new information is then fed back into the ML algorithm, which then suggests a new and improved set of reaction parameters and restarts the automation cycle.

Crucially, the ML method in this work is data-efficient when handling many reaction parameters compared to traditionally used statistical methods, and without bias compared to R&D scientists. This results in a more accurate and sustainable optimisation process that completes in fewer experiments and consumes lower quantities of hazardous chemicals. The knowledge gained from these studies will be transferred back to industry to aid in accelerating production of active pharmaceutical and agrochemical ingredients and minimise this bottleneck in the development cycle when bringing products to market.

Reference:

(1)   Wouters, O. J.; McKee, M.; Luyten, J. Estimated Research and Development Investment Needed to Bring a New Medicine to Market, 2009-2018. JAMA 2020, 323 (9), 844–853.

Mohammed obtained his Master's degree in chemistry from the University of Leeds in 2014, working on the automated development of chemical reactions in continuous flow. Mohammed undertook at a one-year placement at Tata Steel Europe as an environment chemist as part of this programme. Through a subsequent project with a leading fine chemical manufacturer, he designed and built a bespoke flow system for the continuous manufacture of bio-renewable materials. In 2019, Mohammed completed his PhD at the School of Chemical and Process Engineering at the University of Leeds. His research, under the supervision of Dr David Harbottle and Prof. Kevin Roberts, focused on the use of X-scattering and molecular modelling techniques to understand the complex phase behaviour of multi-component synthetic surfactant systems.

Fig. 1: Chemical handling equipment and reactors for automated optimisation.

The PIPS project combines synthetic chemistry, automated process development and machine learning. Find out more on page 122.

Highlighted research outputs from April - September 2020

*A selection of our top publications from across the programme.*

IRP1: Adsorption and diffusion of moisture and wet flue gas on silica gel

Prerna Goyal, Mark Purdue and Shamsuzzaman Farooq. *Chemical Engineering Science*

Abstract: Moisture equilibrium and kinetics on silica gel, a potential adsorbent for drying wet flue gas, are measured using static volumetric and dynamic column breakthrough (DCB) methods. Isotherm models are identified that adequately describe the adsorption branch and hysteresis of the desorption branch. The transport mechanism and transport coefficient of moisture in silica gel pores are also presented. DCB experiments in the silica gel bed pre-equilibrated with wet helium are used to quantify N_2 and CO_2 adsorption reduction in the presence of moisture. Combining present results with those reported recently for equilibrium and transport models for N_2 and CO_2 (Goyal et al., 2019), a ternary simulation model is finally proposed in this study that sufficiently predicts complete adsorption and desorption breakthrough of wet flue gas (N_2, CO_2 and H_2O mixture) in an initially clean silica gel bed. Two mixture equilibrium calculation methods are compared while retaining the independently established transport mechanism.
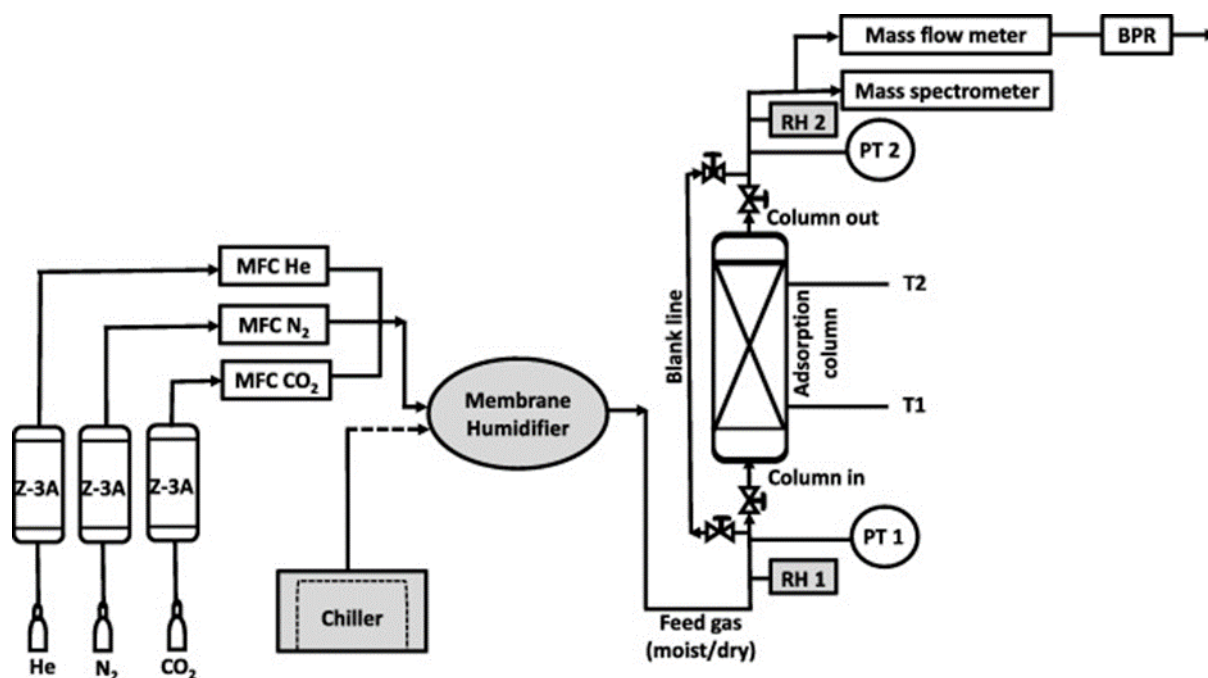

Schematic of the dynamic column breakthrough experimental set up [Z-3A- Zeolite 3A pre-drying columns, MFC- mass flow controller, PT- pressure transducer, T1-T2- thermocouples, RH - relative humidity sensor, BPR- back pressure regulator].

IRP1: Minimalization of metallic Pd formation in Suzuki reaction with a solid-state organometallic catalyst

Bowen Li and Hua Chun Zeng, *ACS Applied Materials and Interfaces*

Abstract: Suzuki reaction usually uses palladium (Pd) complexes to accommodate a wide range of substrates. In pursuing greener synthesis, immobilization of Pd complexes with various support materials has shown promising potential. Although this approach can give stable conversion, initially immobilized Pd ions are largely reduced to Pd0 aggregates and turned essentially into supported nanoparticles after use, which departs from its original intention of complex immobilization and thus hampers its activity. Herein, we immobilize noble metal ions into a spherical thiolated organosilica. This new type of catalysts can catalyze Suzuki reaction homogeneously via leaching out Pd ions and shuttling them back after the reaction. The excellent reusability attained can be attributed to minimalization of forming metallic palladium. Thus, the developed catalysts can be viewed as a two-way device to release and to restore metal ions for homogeneous catalysis.
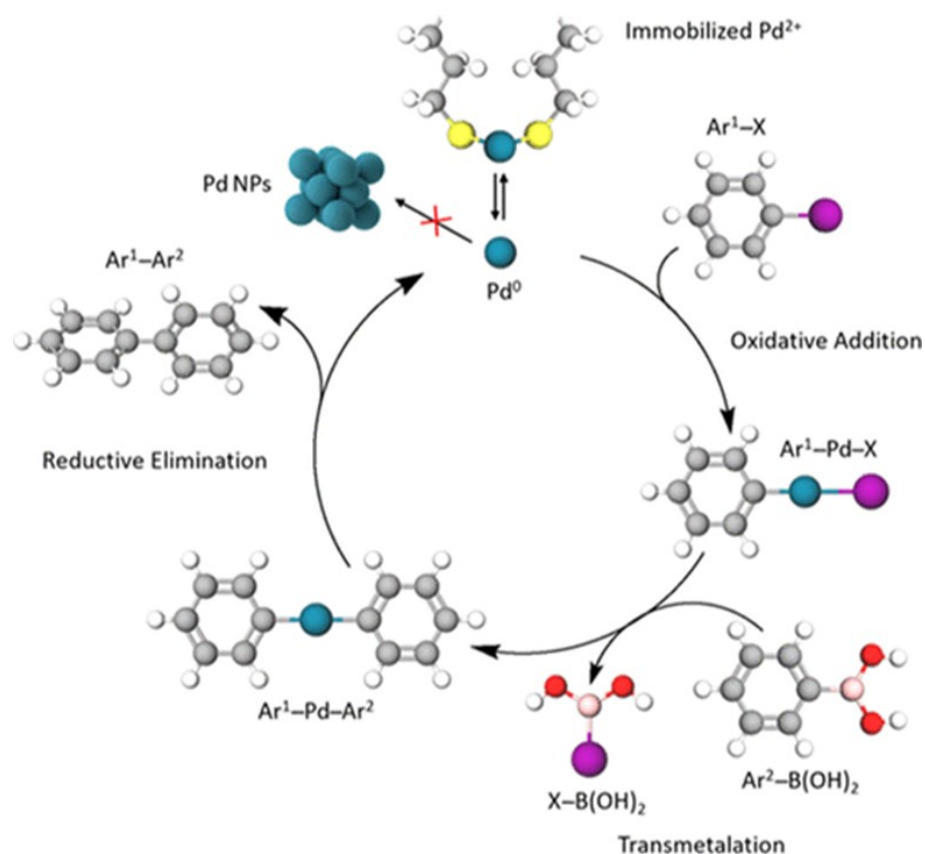
Suzuki reaction mechanism in which the reaction proceeds via the homogeneous route with leached Pd as the active catalyst. Instead of aggregating to Pd nanoparticles, the unsaturated Pd0 after the reaction was reoxidized and shuttled back to reproduce initial thiolated organosilica.

IRP1: Trimetal atoms confined in openly accessible nitrogen-doped carbon constructs for an efficient ORR

Jingjing Wang, Wenjie Zang, Shibo Xi, Mohammadreza Kosari, Stephen J. Pennycook and Hua Chun Zeng, *Journal of Materials Chemistry A*

Abstract: The electrochemical oxygen reduction reaction (ORR) is one of the key processes for various energy storage and conversion systems. To date, transition metal-based nitrogen–carbon systems (M/NC) have been demonstrated as promising low-cost catalysts. However, their low content of metals and the lack of coupling among multimetal atoms still affect the ORR kinetics. Herein, we develop a hierarchical N-doped carbon structure to house isolated trimetal (Co, Fe and Zn) atoms *via* pyrolysis of doped amorphous ZIF-90. Owing to the versatile compositional and structural design of its precursors, the resultant catalyst has a high metal loading (5.5 wt%) and a highly open structure with abundant mesopores, which significantly increase the population of effective active sites. Moreover, charge transfer among these three metals (Co, Fe and Zn) is found, which leads to the promotion of the oxidation state of Co species (primary active sites). Benefiting from the openly accessible active sites and the promotion effect, the catalyst exhibits remarkable ORR activity and stability, outperforming its bimetallic/single metal counterparts and commercial Pt/C.
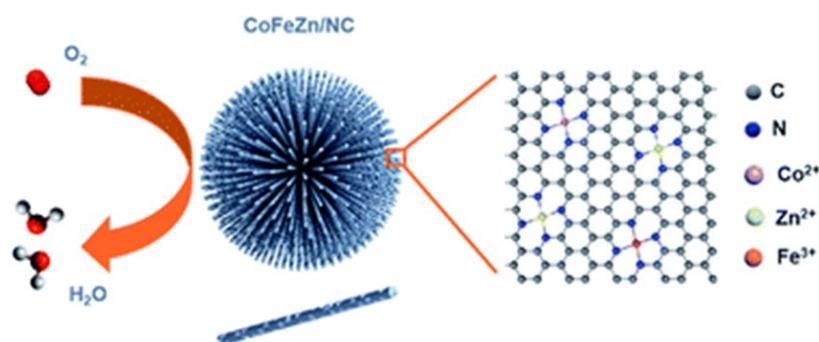
IRP2: A hydrogen/oxygen hybrid biofuel cell comprising an electrocatalytically active nanoflower/laccase-based biocathode

Joseph Yoon Young Lee, Kamal Elouarzaki, Harshjyot Singh Sabharwal, Adrian C. Fisher and Jong Min Lee, *Catalysis Science & Technology*

Abstract: Enzymatic fuel cells (EFCs) are one of the promising next-generation energy conversion systems. However, their applications are often obstructed by their power density and their lack of long-term operational stability. Enzyme immobilization is one of the strategies to overcome these limitations. The construction of a surface-confined electrode architecture that provides biocompatible microenvironments for enzyme immobilization might be a promising approach to address such barriers. Inspired by the interaction between laccase and copper ions leading to the growth of micrometer-sized flower-like particles, we successfully demonstrate a cathodic electrode design using these hybrid nanoflowers as a biocatalyst for oxygen reduction. Using this electrode architecture, enhanced activity and stability are achieved. By integrating this cathode in a fuel cell setup, two H_2/O_2 fuel cell configurations have been constructed: a membraneless fuel cell (MFC) and a proton exchange membrane H_2/O_2 fuel cell (PEMFC) that show enhancement of

the performance. The cell is equipped with an oxygen-reducing laccase–Cu nanoflower/carbon nanotube biocathode and an abiotic anode. The maximum power densities of the H_2/O_2 MFC and PEMFC were 52 μW cm^{-2} and 0.41 mW cm^{-2}, respectively. Remarkably, the H_2/O_2 PEMFC system maintained ~85% of its initial power density for 15 days at room temperature, which was greatly improved when compared with previous fuel cells with different nanostructures. These results allow a great variety of conductive biocompatible cathodes to be used and engineered, opening vast possibilities for the development of bioelectronics and biosensors.
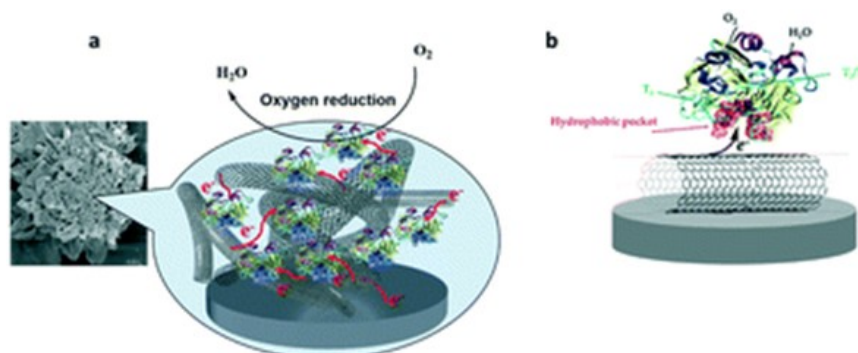
IRP2: Bridging the energy efficiency gap between quasi-neutral and alkaline rechargeable zinc-air batteries by an efficient hybrid battery design

Tianran Zhang, Shengliang Zhang, Sheng Cao, Qiaofeng Yao and Jim Yang Lee, *Energy Storage Materials*
DOI: 10.1016/j.ensm.2020.08.019

Abstract: The large-scale deployment of renewable energy is dependent on the accessibility of cost-effective and long cycle life energy storage solutions. Rechargeable Zn-air batteries are a good candidate, but the aggressiveness of their alkaline electrolyte reduces the battery life. Replacing the alkaline electrolyte with a neutral/quasi-neutral solution is a logical alternative. The energy efficiency of neutral/quasi-neutral Zn-air batteries is however lower than alkaline Zn-air batteries due to the more sluggish kinetics of the oxygen electrochemical reactions in pH-neutral solution. This article describes the development of an efficient hybrid battery design to close the performance gap between alkaline and neutral/quasi-neutral Zn-air batteries. Specifically, a Mn2+-containing electrolyte is used to complement the Zn-air chemistry with a facile MnO2/Mn2+ redox reaction. The quasi-neutral Zn-air battery formulated as such shows a record high round-trip energy efficiency of 63.2% by using only a low-cost phosphated MnO2 oxygen electrocatalyst; which is as energy efficient as the alkaline rechargeable Zn-air batteries but without the cycle life problem of the latter.
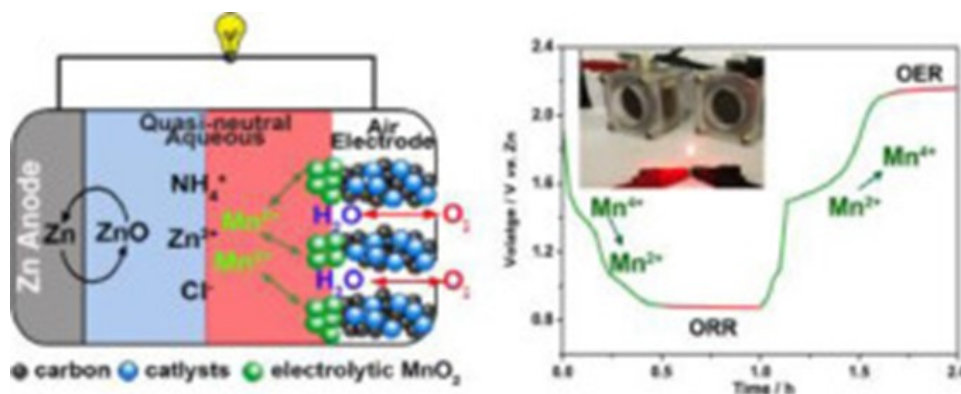
IRP2: A planar, conjugated N4-macrocyclic cobalt complex for heterogeneous electrocatalytic CO₂ reduction with high activity

Xin Wang, Libo Sun, Zhenfeng Huang, Vikas Reddu, Tan Su, and Adrian C. Fisher, *Angewandte Chemie International Edition*

Abstract: Metal complexes have been widely investigated as promising electrocatalysts for CO2 reduction. Most of the current research efforts focus mainly on ligands based on pyrrole subunits, and the reported activities are still far from satisfactory. A novel planar and conjugated N4-macrocyclic cobalt complex (Co(II)CPY) derived from phenanthroline subunits is prepared herein, and it delivers high activity for heterogeneous CO2 electrocatalysis to CO in aqueous media, and outperforms most of the metal complexes reported so far. At a molar loading of 5.93×10−8 mol cm−2, it exhibits a Faradaic efficiency of 96 % and a turnover frequency of 9.59 s−1 towards CO at −0.70 V vs. RHE. The unraveling of electronic structural features suggests that a synergistic effect between the ligand and cobalt in Co(II)CPY plays a critical role in boosting its activity. As a result, the free energy difference for the formation of *COOH is lower than that with cobalt porphyrin, thus leading to enhanced CO production.
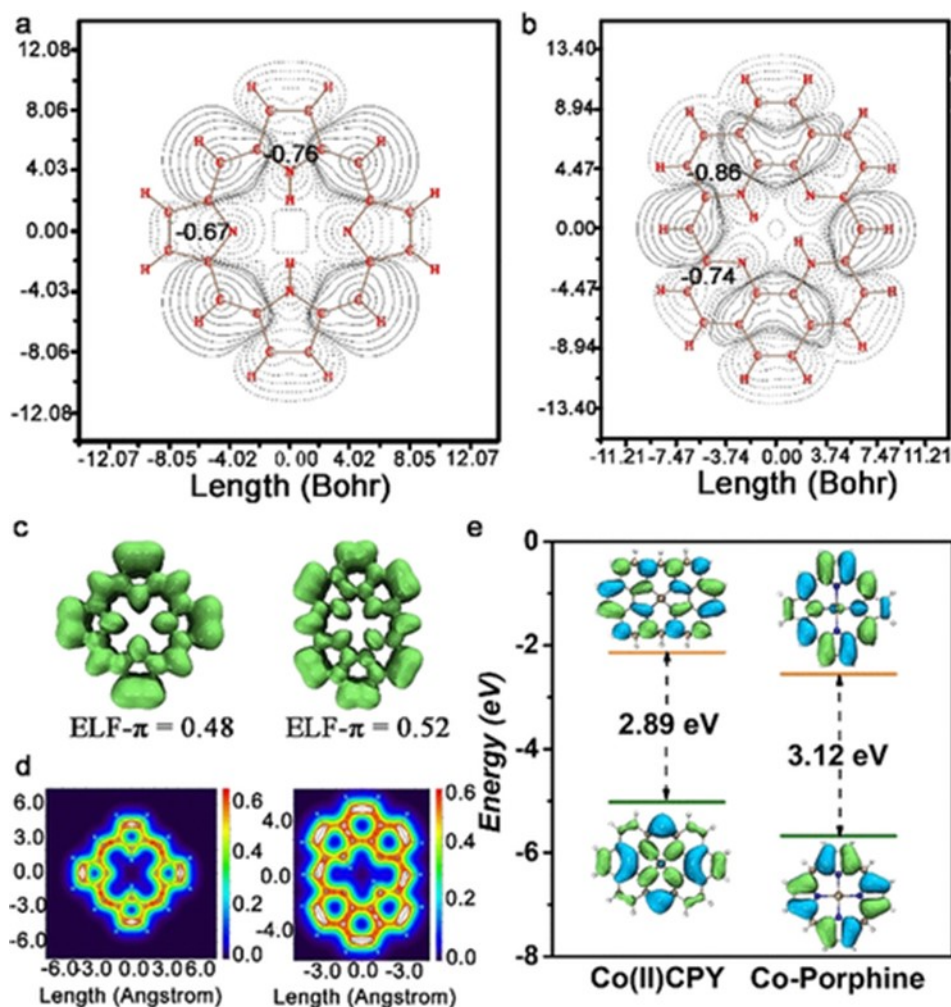
a) The electron density contour map for Porphine (left) and b) H₂CPY (right), respectively (The Mulliken charges of nitrogen atoms are marked out). c) The ELF-π comparison. d) The LOL-π isosurface map. e) The HOMO and LUMO orbitals of Co(II)CPY and Co-Porphine.

IRP3: Exploring the internal structure of soot particles using nanoindentation: A reactive molecular dynamics study

Laura Pascazio, Jacob W. Martin, Kimberly Bowal, Jethro Akroyd and Markus Kraft, *Combustion and Flame*

Abstract: The mechanical properties and internal structure of soot nanoparticles is investigated using reactive molecular dynamics simulations of nanoindenting model soot particles. The particles that are provided as inputs to the simulations are generated using reactive molecular dynamics to create 3D networks of crosslinked coronene, circumanthracene and core-shell mixtures of coronene and circumanthracene. The results of the simulated nanoindentation experiments are analysed as a function of the degree of crosslinking (defined as the number of crosslinks per monomer in the particles), the size and the core-shell structure of the particles. In the case of homoge- neous particles (*i.e.* those without a core-shell structure), the simulations show a unique rela- tionship between the degree of crosslinking (*CL*) and the simulated hardness, Young's modulus and deformation ratio. In the case of particles with a core-shell structure, a unique relationship was only found by considering the core-shell ra- tio and the degree of crosslinking in both the core and the shell. Our results allow for interpretation of the nanoindentation experiments as suggesting crosslinks are present in mature soot particles and preliminary evidence that crosslinks also are present within the interior of soot particles.
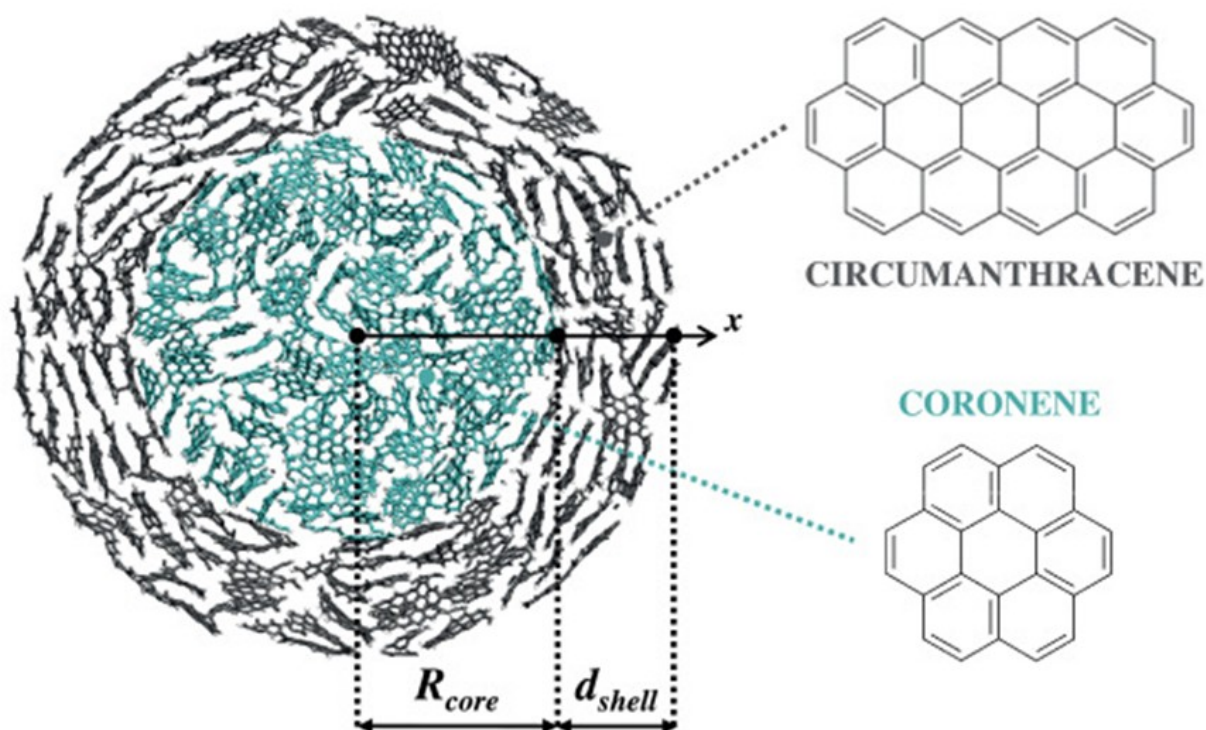

Structure of a model soot particle consisting of a quasi-amorphous core and an ordered outer shell. Blue and grey colours indicate carbon atoms in the core and shell, respectively.

IRP3: Isolated Ni single atoms in nitrogen doped ultrathin porous carbon templated from porous G-C$_3$N$_4$ for high-performance CO$_2$ reduction'

Yan Lu, Haojing Wang, Pengfei Yu, Yifei Yuan, Reza Shahbazian-Yassar, Yuan Sheng, Shuyang Wu, Wenguang Tu, Guanyu Liu, Markus Kraft and Rong Xu, *Nano Energy*

Abstract: Electrochemical reduction of CO$_2$ to value-added products is an effective approach to manage the global carbon balance. However, the lack of effective electrocatalyst for CO$_2$ reduction process is a major obstacle for its development. Currently, constructing atomically dispersed non-precious metal electrocatalysts presents a promising way to build high-performance and cost-effective electrochemical CO$_2$ reduction systems. Herein we demonstrate a novel strategy to realize the anchoring and stabilization of isolated Ni atoms in the nitrogen-doped ultrathin porous carbon nanosheets via a polydopamine-assisted g-C$_3$N$_4$ template method. Benefitting from the abundant atomic Ni sites and ultrahigh specific surface area of porous 2D supports (>1000 m^2 g^{-1}), the catalyst exhibits excellent activity for CO$_2$ reduction with particularly high selectivity towards CO, achieving a faradaic efficiency of 96% at −0.86 V (vs. RHE) with a current density of 26.4 mA cm^{-2} in 0.1 M KHCO$_3$ solution.
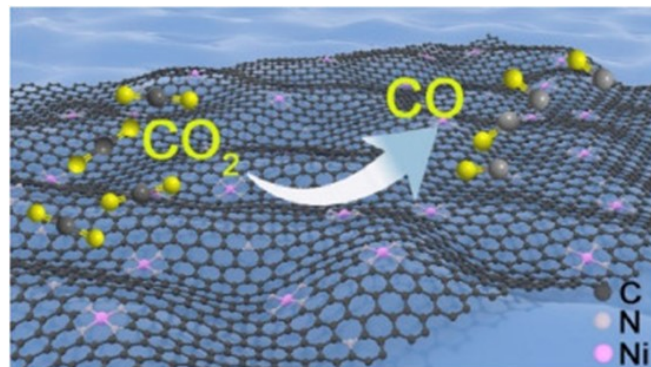
A high-performance CO$_2$ electroreduction catalyst of isolated Ni atoms supported on nitrogen-doped ultrathin porous carbon nanosheets was fabricated via a polydopamine-assisted g-C$_3$N$_4$ template method. By virtue of the highly active Ni–N$_4$ centres and ultrahigh specific surface area of porous 2D supports, it shows excellent activity for CO$_2$ reduction with particularly high selectivity towards CO.

IRP3: The effect of poly(oxymethylene) dimethyl ethers (PODE3) on soot formation in ethylene/PODE3 laminar coflow diffusion flames

Yong Ren Tan, Maurin Salamanca, Laura Pascazio, Jethro Akroyd and Markus Kraft, *Fuel*

Abstract: This paper investigates the effect of poly(oxymethylene) dimethyl ether(PODE$_3$) on soot formation in ethylene/PODE$_3$ laminar coflow diffusion flames. The flames were fuelled using ethylene/PODE$_3$ mixtures, where up to 20% of the total carbon in the mixture was substituted with PODE$_3$. Flame temperature measurements suggest that differences in the soot formation in the flames are more likely due to a chemical effect rather than a temperature effect. Colour ratio pyrometry and differential mobility spectrometry were used to measure the soot volume fraction and the particle size distribution of the flames. PODE$_3$ was observed to be effective in reducing soot formation in previous engine studies. However, for the laboratory flames studied in this work, it was observed that introducing low levels of PODE$_3$ actually increased the amount of soot. When PODE$_3$ was blended with ethylene at 5%, there was an increase of about 10% in the soot volume fraction and about 6% in average particle size compared to the pure ethylene flame. Consideration of the chemical pathways suggests that this interaction is specific to C2 chemistry. Only when the amount of PODE$_3$ was increased to 10% and 20% did the soot volume

fraction and average particle size decrease compared to the pure ethylene flame. The results suggest that blending sufficient amounts of PODE$_3$ with fuels could reduce soot formation, but that the use of too little PODE$_3$ could increase soot formation in the cases of fuels that produce a substantial amount of C2 species in fuel-rich regions of an engine.
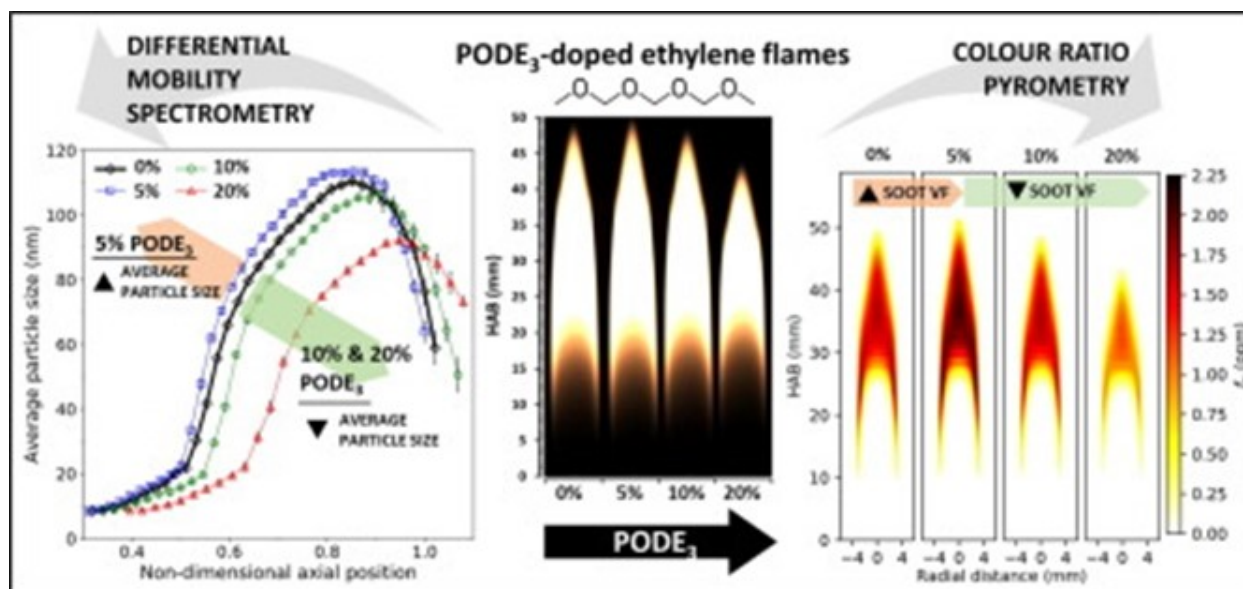
**IRP JPS: OntoPowSys: A power system ontology for cross domain interactions in an eco industrial park**

Aravind Devanand, Gourab Karmakar, Nenad Krdzavac, Rémy Rigo-Mariani, Y.S. Foo Eddy, Iftekhar A. Karimi, and Markus Kraft, *Energy & AI*

Abstract: Knowledge management in multi-domain, heterogeneous industrial networks like an Eco-Industrial Park (EIP) is a challenging task. In this paper, an ontology-based management system has been proposed for addressing this challenge. It focuses on the power systems domain and provides a framework for integrating this knowledge with the other domains of an EIP. The proposed ontology, OntoPowSys is expressed using a Description Logics (DL) syntax and the OWL2 language was used to make it alive. It is then used as a part of the Knowledge Management System (KMS) in a virtual EIP called the J-Park Simulator (JPS). The advantages of the proposed approach are demonstrated by conducting two case studies on the JPS. The first case study illustrates the application of optimal power flow (OPF) in the electrical network of the JPS. The second case study plays an important role in understanding the cross-domain interactions between the chemical and electrical engineering domains in a bio-diesel plant of the JPS. These case studies are available as web services on the JPS website. The results showcase the ad-

vantages of using ontologies in the development of decision support tools. These tools are capable of taking into account contextual information on top of data during their decision-making processes. They are also able to exchange knowledge across different domains without the need for a communication interface.
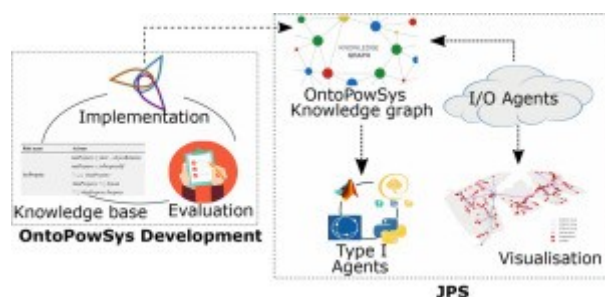
IRP JPS: A Smart Contract-based agent marketplace for the J-Park Simulator - a knowledge graph for the process industry

Xiaochi Zhou, Mei Qi Lim and Markus Kraft, *Computers & Chemical Engineering*

Abstract: The chemical industry is increasingly relying on agents for data acquisition, optimization, and simulation. In order to enable efficient management of agents, Knowledge Graphs (KG) together with agent composition frameworks are therefore applied. However, a method to assess the reliability of agents for such systems is absent. Therefore, this paper proposes a Smart Contract-based agent marketplace for composition frameworks to estimate the reliability of agents. In this agent marketplace, we improved the feedback-based reputation system by leveraging Smart Contracts to eliminate fraudulent ratings and to enable automation. The marketplace incorporates a rating-dependent payment mechanism as well, to further enhance trust. The paper also illustrates how this marketplace is integrated into the J-Park Simulator (JPS) agent composition framework for the automated agent selection and transaction.

A screenshot of the visualisation of the air dispersion simulated by the composite agent.

IRP JPS: A Parallel World Framework for scenario analysis in knowledge graphs

Andreas Eibeck, Arkadiusz Chadzynski, Mei Qi Lim, Kevin Aditya, Laura Ong, Aravind Devanand, Gourab Karmakar, Sebastian Mosbach, Raymond Lau, Iftekhar A. Karimi, Eddy Y. S. Foo and Markus Kraft, *Data-Centric Engineering*

Abstract: This paper presents Parallel World Framework as a solution for simulations of complex systems within a time-varying knowledge graph and its application to the electric grid of Jurong Island in Singapore. The underlying modeling system is based on the Semantic Web Stack. Its linked data layer is described by means of ontologies, which span multiple domains. The framework is designed to allow what-if scenarios to be simulated generically, even for complex, inter-linked, cross-domain applications, as well as conducting multi-scale optimizations of complex superstructures within the system. Parallel world containers, introduced by the framework, ensure data separation and versioning of structures crossing various domain boundaries. Separation of operations, belonging to a particular version of the world, is taken care of by a scenario agent. It encapsulates functionality of operations on data and acts as a parallel world proxy to all of the other agents operating on the knowledge graph. Electric network optimization for carbon tax is demonstrated as a use case. The framework allows to model and evaluate electrical networks corresponding to set carbon tax values by retrofitting different types of power generators and optimizing the grid accordingly. The use case shows the possibility of using this solution as a tool for CO_2 reduction modeling and planning at scale due to its distributed architecture.
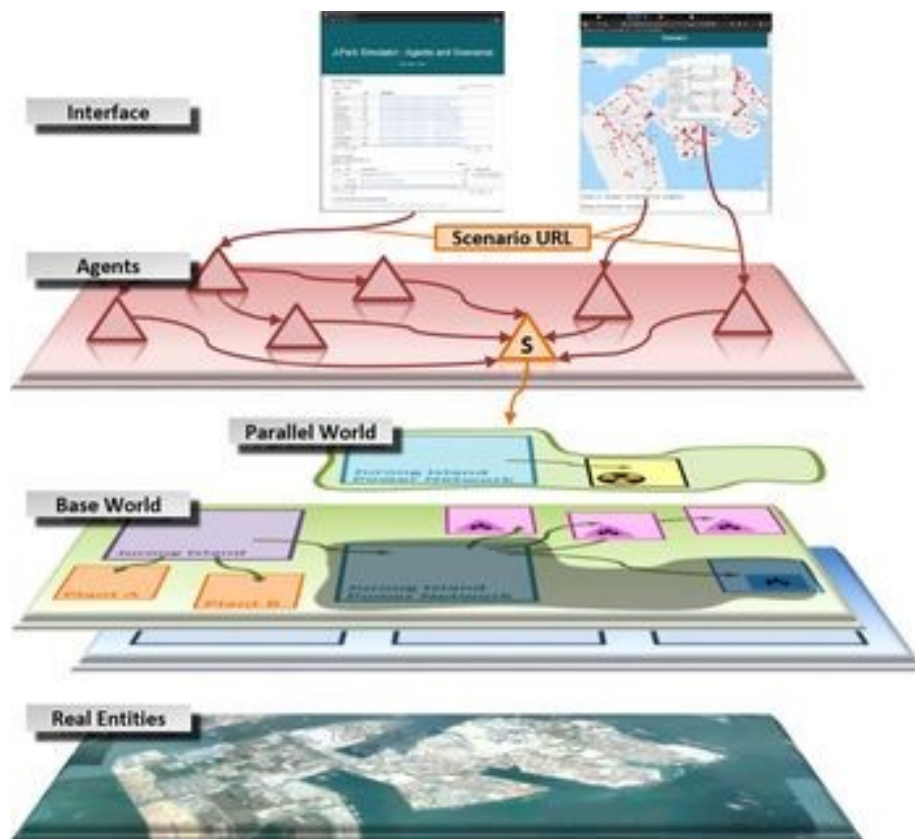
Breakdown of the World representation layers in the J-Park Simulator system (map data ©Google).

eCO₂EP: Photocatalytic NOx Abatement: Recent Advances and Emerging Trends in the Development of Photocatalysts

Nguyen, Van-Huy, Ba-Son Nguyen, Chao-Wei Huang, Thi-Thu Le, Chinh Chien Nguyen, Thi Thanh Nhi Le, Doyeon Heo, Quang Viet Ly, Quang Thang Trinh, Mohammedreza Shokouhimehr, Chanlei Xia, Su Shiung Lam, Dai-Viet N. Vo, Soo Young Kim and Quyet Van Le, *Journal of Cleaner Production*

Abstract: The abatement of NOx emission, which is one of the most critical global environmental issues, is traditionally addressed using risky and costly approaches that require high reaction temperatures. To counter this drawback, much attention has been directed at the development of photocatalytic NOx abatement techniques, including photocatalytic oxidation, photocatalytic decomposition, and photo-selective catalytic reduction (photo-SCR), as they allow one to reduce the reaction temperature and increase conversion efficiency. Therefore, photocatalyst design is of crucial importance for the development of next-generation NOx abatement technologies. This review rationally summarizes and discusses recent progress in photocatalytic NOx abatement, highlighting catalyst type, removal pathway, and parameters governing the removal efficiency for each approach as well as considering strategies for the advancement of photocatalysts featuring high catalytic activities at low reaction temperatures for each process. Finally, the remaining challenges obstacles and directions for the future development of photocatalytic NOx abatement are provided.
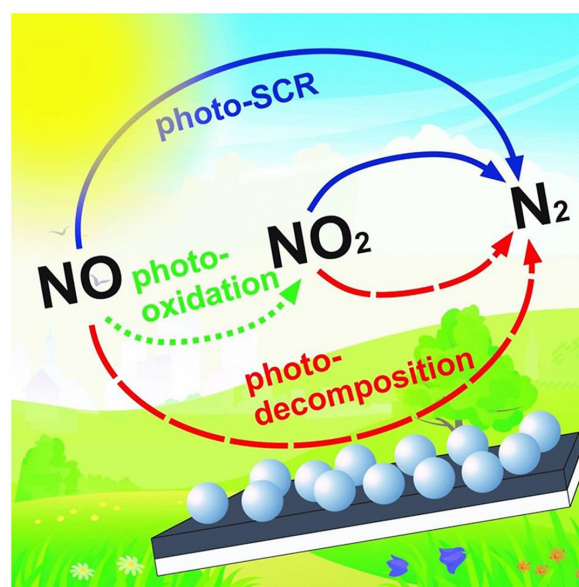
IRPs 1 and 3: The role of NO₂ and NO in the mechanism of hydrocarbon degradation leading to carbonaceous deposits in engines

Radomir I. Slavchov, Maurin Salamanca, Danilo Russo, Ibrahim Salama, Sebastian Mosbach, Stuart M. Clarke, Markus Kraft, Alexei A. Lapkin and Sorin V. Filip, *Fuel*

Abstract: A hypothetical mechanism of degradation of the fuel droplet leaking out from the injector nozzle in a direct injection combustion engine has been proposed recently. This involves as a key step a radical chain oxidation initiated by NO₂ and branched by nitric oxide, NO, both produced by the combustion. The degradation causes the formation of injector nozzle carbonaceous deposits. The present work gives an experimental validation of some of the assumptions behind this model. An autoclave is used to oxidize isooctane under conditions relevant to the cylinder wall near the nozzle (~150 °C, 10 bar, 5% O₂, 100 ppm of NO₂ by mole and 500 ppm NO in the gas phase), and the degradation products are monitored via gas chromatography-mass spectrometry (GC–MS). The results show no observable fuel degradation in the absence of NOₓ. NO appears to be able to initiate a radical chain by producing NO₂. Nitric oxide also alters the radical chain by transforming the alkyl peroxy radicals (ROO·) to more reactive alkoxy radicals (RO·), resulting in a

range of different products. In addition, NO tends to terminate the radical chain by neutralizing a fraction of the alkyl peroxy radicals, producing alkyl nitrates as termination products. The existence of a radical chain is supported by demonstrating the antioxidative action of a radical scavenger. The chemical reaction mechanism is investigated, based on the detected products, and the key species involved in the degradation process are identified.

Reaction mechanism of isooctane and oxygen – main reactions. The key alkyl radicals formed are in blue.
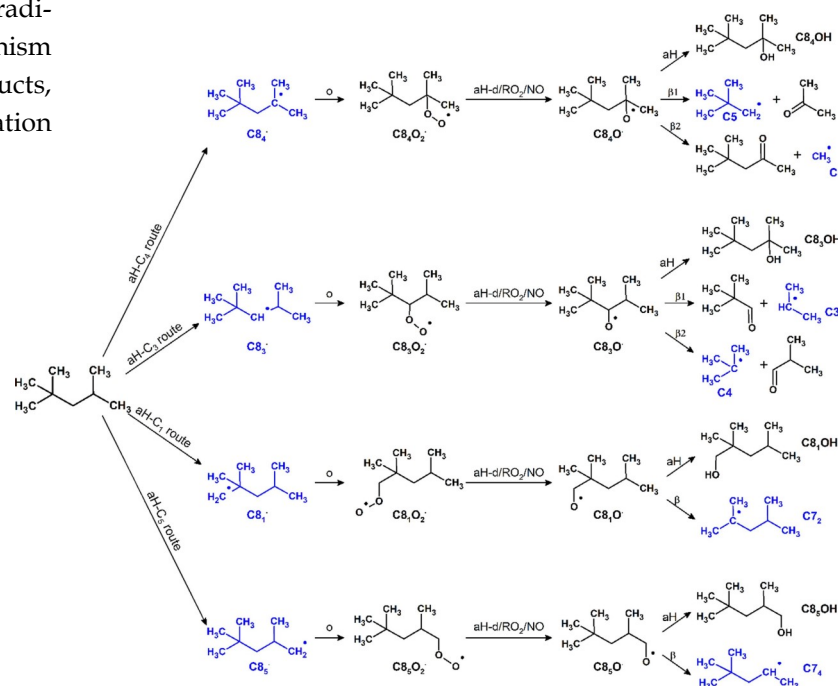

eCO₂EP and IRP2: Porous-organic-polymer-triggered advancement of sustainable magnetic efficient catalyst for chemoselective hydrogenation of cinnamaldehyde

Ratul Paul, Chitra Sarkar, Yong Yan, Quang Thang Trinh, Bolla Srinivasa Rao, Chih-Wen Pao, Jyh-Fu Lee, Wen Liu and John Mondal, *ChemCatChem*

Abstract: In this study, we adopted a cost-effective, facile and metal & template-free strategy for the successful synthesis of hydroxyl enriched POP (denoted as TPT). An integrated catalyst, Pd−Fe₃O₄@TPT, has been developed for the liquid phase selective hydrogenation cinnamaldehyde (CAL). Pd−Fe₃O₄@TPT exhibited excellent catalytic performance, providing 100 % selectivity towards hydrocinnamaldehyde (HCAL) under mild reaction conditions (with relatively low hydrogen pressure and very short reaction time), whereas Fe₂O₃@TPT appeared inert. Compared with the conventional catalytic systems, our newly designed catalyst was superior in many aspects, owing to the rigid nature of TPT-POP, which prevents aggregation and leaching of the metal nanoparticles.
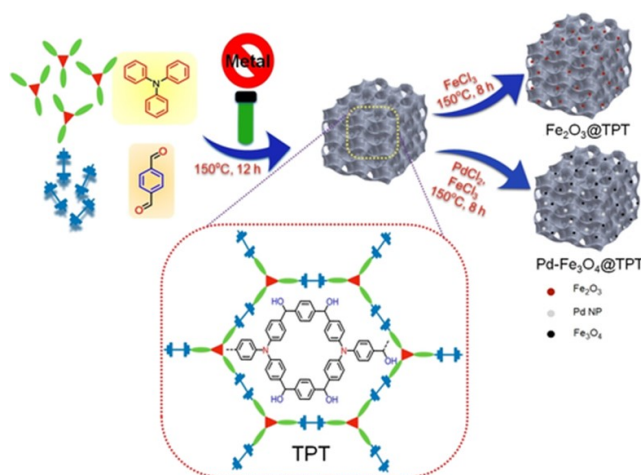
Schematic Illustration for the synthesis of Porous-Organic-Polymer and the sequential synthetic approach for Pd−Fe₃O₄ based integrated catalyst.

SUSTAINABLE REACTION ENGINEERING FOR CARBON NEUTRAL INDUSTRY

IRP1 is focused on chemical technologies that allow rapid decarbonisation 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

Phase 2 of IRP1 is developing along three main directions: new structured nanomaterials for C1 feedstocks conversion and their scale up to industrially-relevant catalytic systems, development of new transformations for conversion of bio-waste streams into higher-value products, and engineering of catalytic processes for reduction of carbon emissions.

In the last period the IRP1 projects have significantly progressed in developing new unique capabilities in building catalytic nano-architectures, in developing novel oxygen carrier materials, in scaling up synthesis of nanomaterials and identifying new potentially high-impact transformations of bio-feedstocks. The recent (September 2020) IRP1 workshop highlighted these achievements and identified new collaborations within IRP1 groups and also the potential for developing high-impact ambitious projects, addressing the more challenging issues in the topics of C1 activation, CO_2 utilisation and bio-waste utilisation.

Professor Alexei Lapkin, PI
University of Cambridge

Update on work package 1.1
Design of nano-structured catalysts

In the previous report, **LI Bowen (Research Engineer, NUS)** and **Prof. ZENG Hua Chun (PI, NUS)** presented the preparation of hollow ZSM-5 crystals with functionalised interior (CuZn) and exterior (Pt) (Figure 1.1a). For the past months, this catalyst has been further evaluated for direct conversion of CO_2 to C_{2+} hydrocarbons. In particular, acidic sites of ZSM-5 could further catalyse the conversion of methanol to olefins while its precisely engineered pore structure prevents the formation of long chain hydrocarbons. In addition, the metal-support interaction prevents aggregation of both CuZn and Pt nanoparticles. The Pt nanoparticles, located on the exterior surface of ZSM-5, are well-known catalysts for producing CO during CO_2 hydrogenation. The inclusion of Pt on the exterior surface was believed to partially hydrogenate the CO_2 to CO when the reactants diffuse into the ZSM-5 crystal and get converted to methanol by CuZn nanoparticles. As such, Pt was used to provide a confined environment with enhanced CO concentration.

We have also explored the possibility of introducing noble metals into the hollow ZSM-5. In this attempt, we have prepared hollow ZSM-5 with only Cu nanoparticles imbedded as sacrificial precursor (Figure 1.1b). Spatially controlled deposition of Pd via galvanic replacement reaction was achieved (Figure 1.1c). The catalyst was first reduced in H_2 gas to produce metallic Cu. In this galvanic replacement, the transition metal was oxidised and dissolved into solution as ions while the Pd^{2+} precursor was reduced to a metallic state, forming Pd nanoparticles only at Cu imbedded locations. Polyvinylpyrrolidone was also added to prevent Pd forming in the solution, which will likely deposit onto ZSM-5 exterior surface. Using ICP-OES technique, the Pd loading was measured to be 0.36 wt%. A representative of selective hydrogenation of 4-vinylphenol is presented in Figure 1.1d.
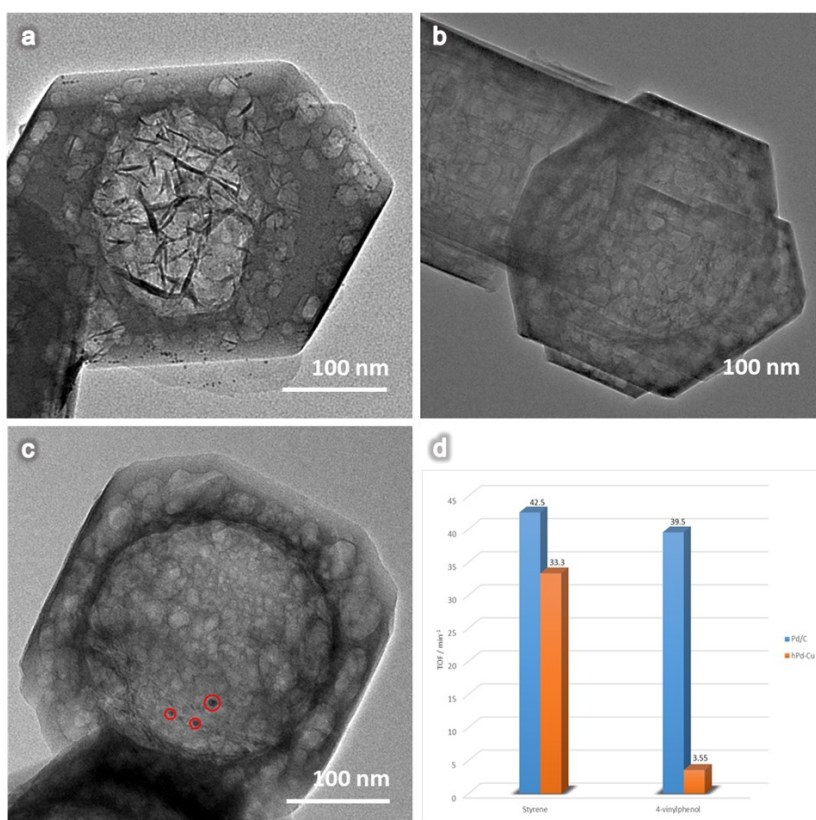

Fig. 1.1: Representative FETEM images of (a) hollow ZSM-5 crystals with functionalised interior (CuZn) and exterior (Pt); (b) hollow ZSM-5 crystals with only Cu in the interior and (c) hollow ZSM-5 crystals with Pd (labelled with red circles) deposited in the interior via galvanic replacement reaction; and (d) size selective hydrogenation reaction with hCu-Pd catalyst. The bulkier 4-vinylphenol has suffered a great TOF drop for hollow ZSM-5 confined Pd catalyst.

WANG Jingjing's (Research Associate, NUS) main research interest lies in the design and synthesis of novel electrocatalysts for water electrolysis and CO_2 reduction. In the last six months, she prepared a heterostructure coupling mesoporous hollow sphere of N, P-doped carbon (meso-NPC) with ultrafine Co_2NiO_x nanoparticle, named as meso-NPC/Co_2NiO_x. The meso-NPC hollow spheres were first fabricated via a novel nanocasting method using mesoporous SiO_2 as the "mould" and the atomic ratio of P in the meso-NPC can be tuned by controlling the amount of one of the filling organics, etidronic acid. Due to the large surface area and abundant surface hydroxyls, the meso-NPC formed strong bonding with the Co_2NiO_x nanoparticles (< 2 nm in size)

loaded on it. Serving as an OER electrocatalyst, the heterogeneous meso-NPC/Co_2NiO_x shows great working enhancement compared to its single-component counterparts. Through further mechanism study by X-ray photoelectron spectroscopy, a strong effect of electron transfer is found from the Co_2NiO_x to the meso-NPC, which leads to increases in oxidation state of transition metals. Most importantly, we also reveal that the increase of the amount of P dopant in the meso-NPC/Co_2NiO_x system can efficiently facilitate this metal-to-support charge transfer, which also implies that the biphasic interaction between the Co_2NiO_x nanoparticles and the meso-NPC hollow spheres generates active catalytic sites of both TM–N–C and TM–P–C surface species.
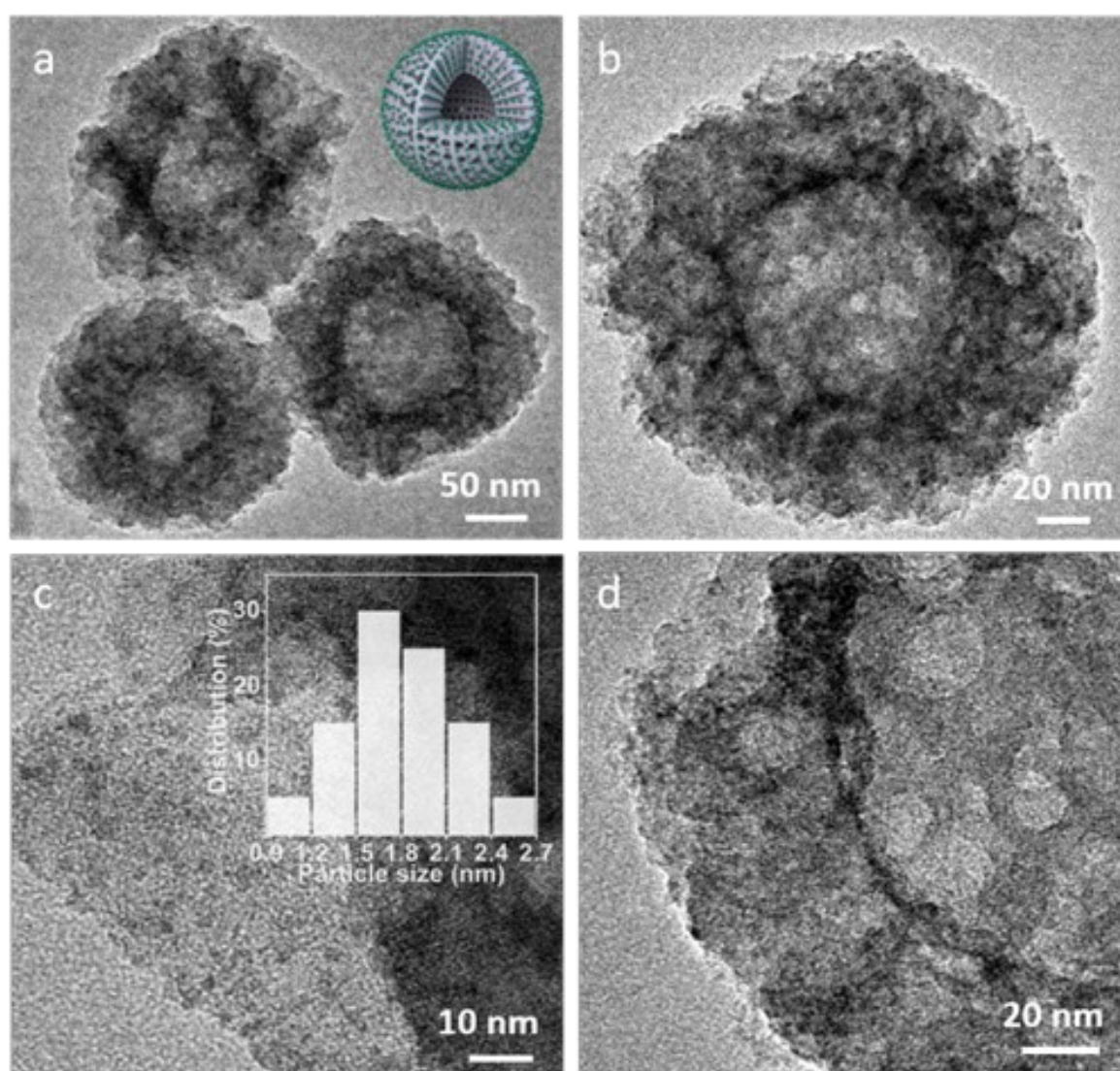

Figure 1.2: TEM images with different magnifications (a-c) of meso-NPC/Co_2NiO_x (Inset of (c): the profile of particle size distribution of Co_2NiO_x); (d) Sectional view image.

WANG Jingjing

In the previous progress report, **Alvin LIM Ming Hao (PhD student, NUS)** and **Prof. ZENG Hua Chun** found that excessive iron (II) nitrate in the mixed nickel (II) and iron (II) nitrate solution causes morphological destruction to the calcined MgAl-LDH nanoflowers. Hence, the calcined MgAl-LDH was further doped with active catalytic materials in reduced or with no iron (II) nitrate, in the mixed nitrate solution, and their CO_2 hydrogenation performance was evaluated. From our results, it was found that the calcined MgAl-LDH doped with just Ni, without any Fe, results in the highest conversion at the same catalyst mass as well as methane selectivity at high pres-sure. Before reduction and reaction, for example, LDOH-10Ni sample has its all metallic elements well-dispersed in the flowerlike LDH nanostructure (see Figure 1.3a). After reaction, the Ni nanoparticles formed were monodisperse and generally much smaller than 20 nm (see Figure 1.3b). Elemental mapping confirms dark particles corresponds to Ni clusters. SEM imaging reveals that bulk catalytic material to be multiple nanoflowers that can be packed into a maze-like structure (see Figure 1.3c). As with the trend in our previous report, CH_4 production significantly increases when reaction temperature is above 300 °C across all the as-synthesised catalysts (see Figure 1.3d).
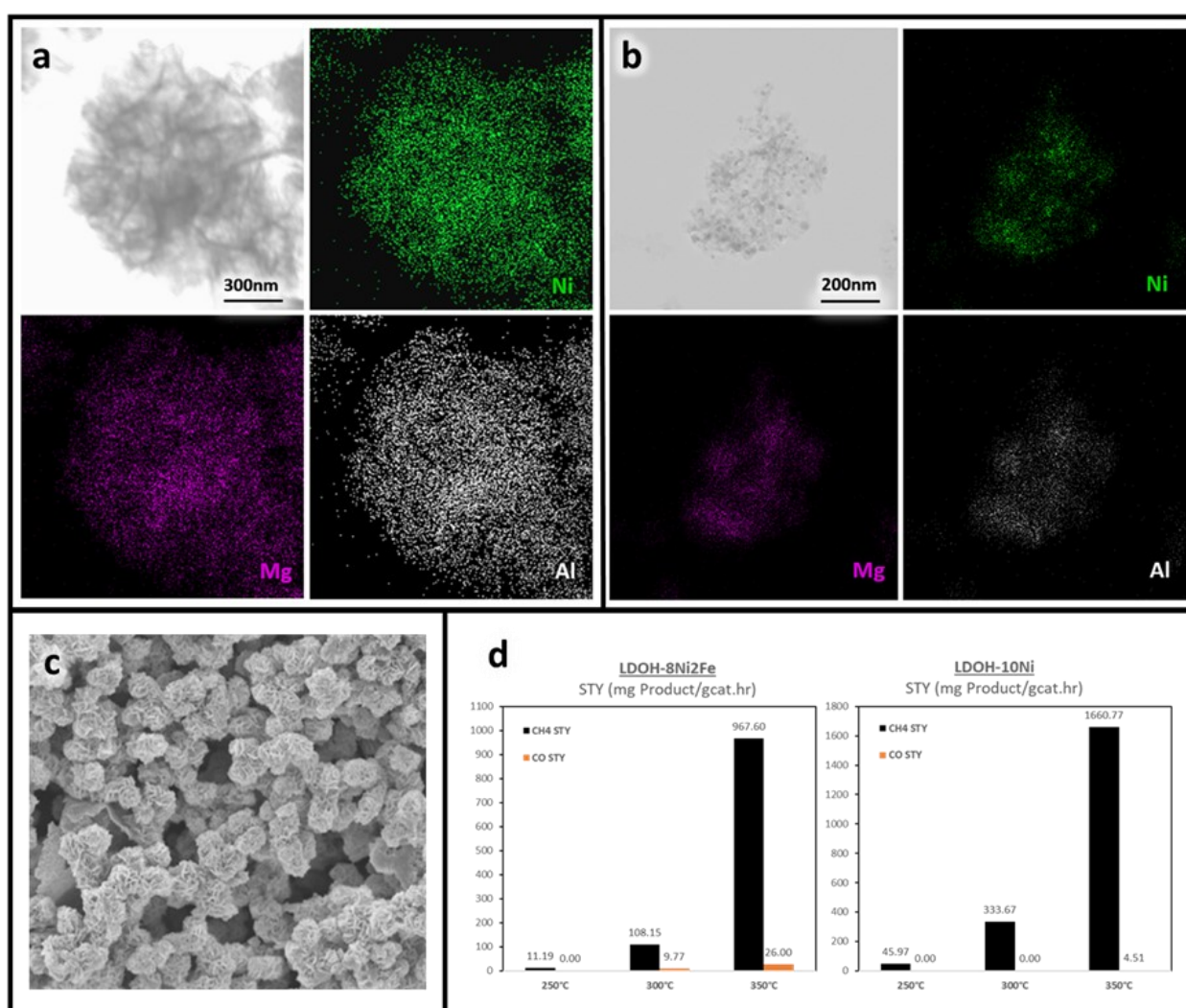

Fig. 1.3: (a) STEM and elemental mappings of LDOH-10Ni, (b) STEM of and elemental mappings of reacted LDOH-10Ni, (c) SEM of LDOH flowerlike catalysts, and (d) Space Time Yield (STY) of CH_4 and CO products of two studied catalysts (LDOH-10Ni and LDOH-8Ni2Fe) at 30 bar.

Alvin LIM Ming Hao

Confirmation of Suzuki-Miyaura Cross-Coupling Reaction Mechanism through Synthetic Architecture of Nanocatalysts

BO Sun, Lulu NING and Prof. ZENG Hua Chun report that Suzuki-Miyaura Cross-Coupling is one of the most versatile reactions for organic synthesis. Despite widespread use of heterogeneous Pd catalysts in Suzuki-Miyaura coupling reactions, detailed roles of Pd, especially the nature of its active species are still a topic of controversy debate for more than four decades. In this project, we use microporous Stöber silica as a membrane to separate the soluble Pd species from solid Pd and conduct size-selective reactions which allow the passage of leaching Pd species, but not of reactants or products larger than the membrane aperture. With this strategy, we have been able to differentiate the surface reaction from the solution cross-coupling. We find that the leached Pd species are the only genuine catalytic intermediate in the cross-coupling reactions. We also confirm that oxidative addition of aryl halides to the solid Pd leads to leaching of the soluble Pd species which is necessary to promote Suzuki-Miyaura reactions (Figure 1.4).
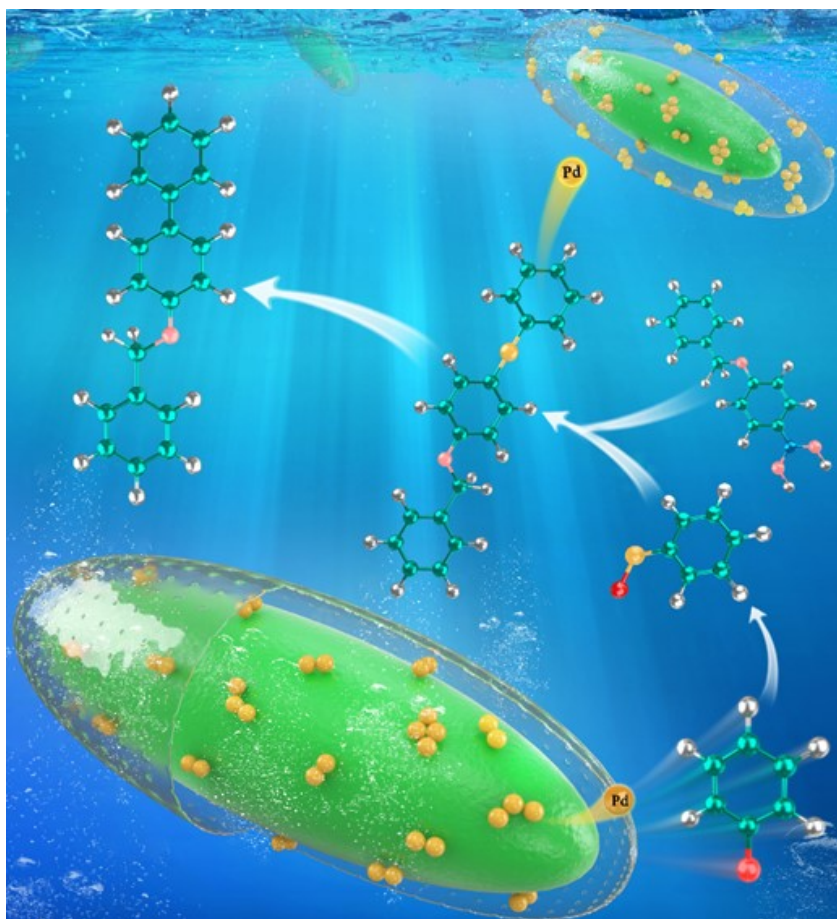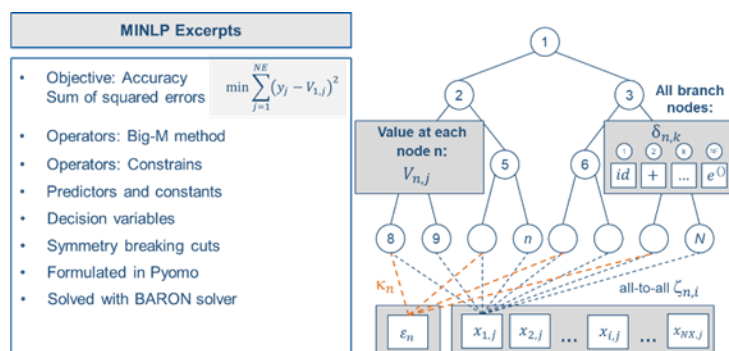

Fig. 1.4: Graphical illustration of the confirmed reaction mechanism of Suzuki-Miyaura cross-coupling (Journal of the American Chemical Society, Vol. 142 (2020) pp. 13823-13832).

Update on work package 1.2
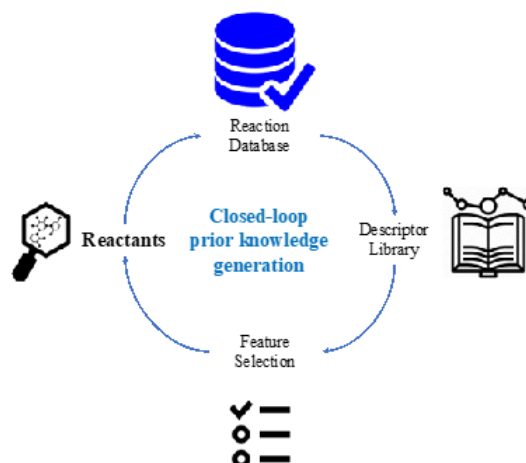## Novel reactions and functional molecules

Liwei CAO's (PhD student, CAM) research topic lies in accelerating product and process design by combining artificial intelligence and a robotic experimental platform. Liwei Cao is currently working on revealing a physical model from a complex system, which is interpretable and transferable compared to a black-box surrogate model. A new MINLP formulation of symbolic regression was proposed for physical model identification. It has been successfully applied on kinetic model identification and will be applied for further complex systems.

Fig. 1.5: Automated prior knowledge generation to select relevant parameters for a given reaction.

Perman JORAYEV

Perman JORAYEV (PhD student, CAM) has been working on improving the ways to enhance process development in pharmaceutical industry. The project requires both computational and experimental work. On the computational side, the first step is to collect relevant data for a given reaction (e.g. amination) from existing reaction databases. Then, the raw data goes through rigorous processing and cleaning to remove unnecessary information. Once the data is cleaned and formatted, the third step is to generate chemical knowledge (e.g. descriptors) for the given reactants, reagents, catalysts, and solvents in the data. Perman Jorayev has recently focused on the aforementioned steps. The next step of this work is to implement machine learning models (e.g. random forest, SVM) to extract relevant features (i.e. reaction parameters) to optimise for yield. These selected parameters will then be used to develop a robust model for the selected case study. Experimentally, Perman Jorayev has been working on validating the automated experimental setup. Due to the difficulty of the reaction (e.g. air and water sensitivity of reagents, pumping suspension using Vapourtec), it requires thorough purification of solvents to be used for the study and validation of accuracy of pumping suspension through the photochemical reactor. Perman Jorayev has finished purifying solvents, testing the experimental setup for handling suspension, and calculating solubilities of co-catalysts for the reaction. Next step of the project is to start collecting training dataset for model development.

Update on work package 1.3
Novel reactors and process technology

Prerna GOYAL's (PhD student, NUS) research project aims to study detailed techno-economic assessment of carbon capture and concentration (CCC) from wet flue gas emitted from a coal fired power plant by Vacuum Swing Adsorption (VSA) process using Silica gel for drying wet flue gas and Zeolite-13X as the adsorbent for CCC from the dried flue gas. She incorporated the experimentally validated equilibrium and kinetic models of the wet flue gas components on silica gel in the VSA process simulator to study the drying process and validated it with VSA experiments for drying wet flue gas on silica gel. The VSA simulator has the flexibility to simulate wet flue gas drying as well as CCC from dry flue gas by linking to the appropriate adsorption equilibrium and mass transfer models. She employed the separately validated simulation model for wet flue gas drying as well as CCC from dry flue gas, for scale-up design and cost analysis of the drying and CCC units. She adopted a costing methodology to study the effect of different operating and performance parameters on the process cost which has led to a clearer understanding of the trade-off between plant size and process cost.
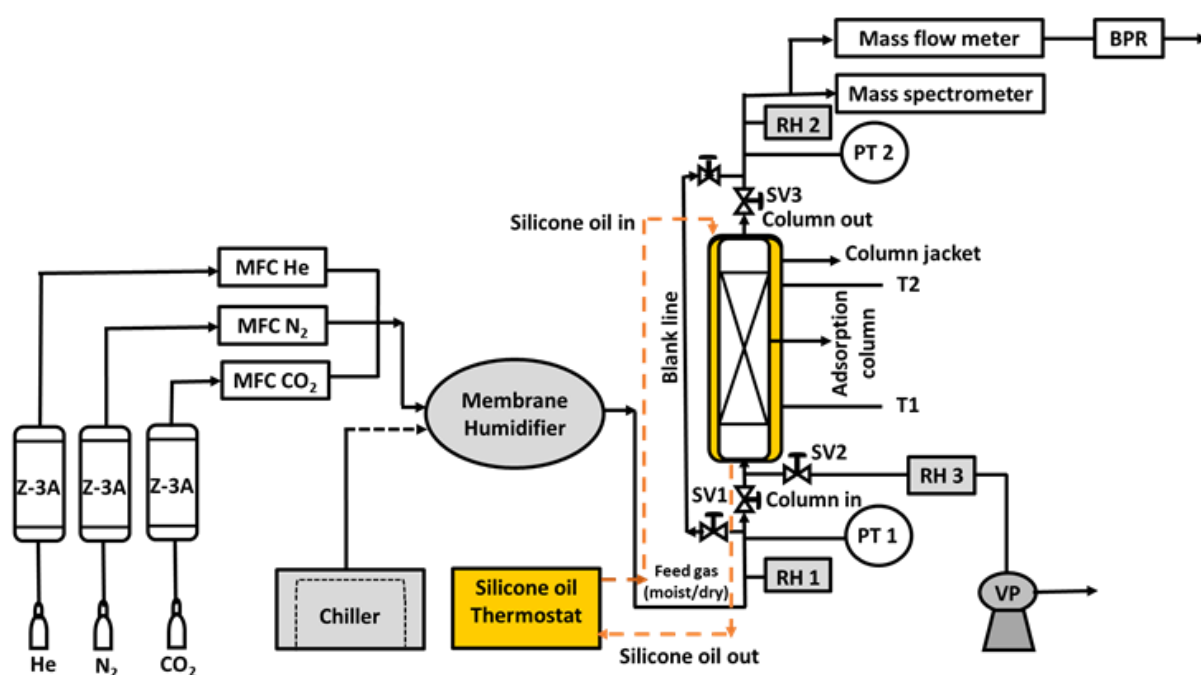

Fig. 1.6: Schematic of the experimental set up [Z-3A- Zeolite 3A pre-drying columns, MFC-mass flow controller, PT- pressure transducer, T1-T2- thermocouples, RH - relative humidity sensor, BPR- back pressure regulator, SV - solenoid valves, VP- vacuum pump].

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 17.

Transformation of Stöber silica spheres to hollow nanocatalysts

Mohammadreza Kosari, Armando Borgna and Hua Chun Zeng, *ChemNanoMat*

Abstract: The discovery of silica spheres by Werner Stöber and his team (known as Stöber silica) has been instrumental to many technological fields such as hollow materials research. Recent research endeavors on (physical and chemical) transformation of Stöber silica have specifically opened up a new horizon in this domain, especially in catalysis science and catalyst technology. Deliberate introduction of working spaces into Stöber silica *via* such transformations is regarded as a meaningful methodology toward fabrication of highly confined hollow nanostructures in the form of *"reactor-like nanocatalysts"* or *"catalyst-like nanoreactors"*. More importantly, advanced catalytic devices with well-defined size, shape, composition, and hollowness could be obtained by these viable approaches. Concerning the further research, the present minireview gives an overview on recent advances about the synthesis and applications of hollow nanocatalysts derived from Stöber silica spheres. Firstly, we will provide the gist of current status of hollow materials research. Secondly, applicable methods for transformation of Stöber silica spheres to hollow nanostructures and hollow nanocatalysts will be elaborated. The stability and durability of SiO_2-based hollow constructs will also be elucidated. Subsequently, research snapshots of Stöber SiO_2-derived hollow nanostructures and their applicability mainly for catalytic purposes, from our research group and literature, will be discussed. Our personal perspectives on promising research opportunities and challenges in this field will also be given at the end.

### Synthesis of mesoporous copper aluminosilicate hollow spheres for oxidation reactions

Mohammadreza Kosari, Abdul Majeed Seayad, Shibo Xi, Sergey M. Kozlov, Armando Borgna and Hua Chun Zeng, *ACS Applied Materials & Interfaces*

Abstract: Hollow functional metal silicate materials have received the most interest due to their large inner space, permeable and functional shell, lighter density, and better use of material compared to their solid counterparts. While tremendous success has been made in the synthesis of individual metal silicates with uniform morphology, the synthesis of multiphase hollow silicates has not been explored yet, although their direct applications could be promising. In this study, mesoporous aluminosilicate spheres (MASS) are transformed to submicrometer copper aluminosilicate hollow spheres (CASHS) via a one-pot hydrothermal process. CASHS has a hollow interior with Cu–Al–Si thorn-like moieties in a lamellar structure on its outer shell. The structure and morphology of CASHS are unique and different from the previously reported tubular copper silicates that are emanated from Stöber silica spheres.

Herein, we also demonstrate that the extent of hollowing in CASHS can be attained by controlling the aluminum content of pristine MASS, highlighting the existence of parameters for in situ controlling the shell thickness of hollow materials. The application of CASHS as a potential heterogeneous catalyst has been directed to important oxidation processes such as olefin oxidation and the advanced oxidation process (AOP).
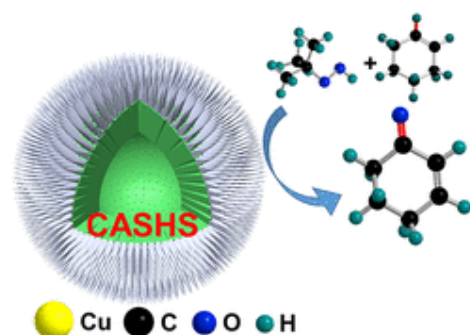
In cyclohexene oxidation, for instance, high selectivity to cyclohex-2-en-1-one is achieved under moderate conditions using *tert*-butyl hydroperoxide as the oxidant. CASHS is a robust heterogeneous catalyst and recyclable for this reaction. CASHS-derived catalysts also favor AOP and enhance the removal of cationic dyes together with H_2O_2 through an adsorption–degradation process.
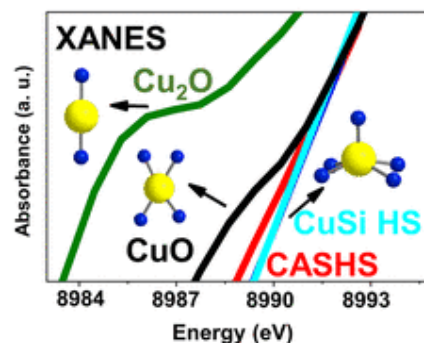

Design of hollow spherical Co@hsZSM5@metal dual-layer nanocatalysts for tandem CO_2 hydrogenation to increase C_{2+} hydrocarbon selectivity

Kelvin Mingyao Kwok, Luwei Chen and Hua Chun Zeng in *Journal of Materials Chemistry A*

Abstract: A thin hollow shell nanostructure can increase effectiveness of zeolites while allowing metal nanoparticles to be supported on both its inner and outer surfaces. Herein, nanoscale hollow spherical ZSM-5 (hsZSM5) shells were synthesized from sub-micron silica spheres through a dissolution–recrystallization mechanism with assistance of a positively charged polymer. The as-prepared hsZSM5 can function as a spacer: different metals (M_n) can be preferentially separated by the thin shell of hsZSM5, making the derived M_1@hsZSM5@M_2 suitable for tandem reactions. The dual-layer Co@hsZSM5@Pt shows higher resistance to metal sintering and alloying in tandem hydrogenation of CO_2 (*i.e.*; reverse water gas shift reaction followed by Fischer–Trøpsch reaction) to short-chain hydrocarbons, which can be used as an alternate clean feedstock to pro

duce chemicals such as olefins, aromatics and polymers. Hydrocarbon selectivity of C_{2+} can be increased up to 46% in Co@hsZSM5@Pt, which was not observed in co-impregnated Pt–Co catalyst.
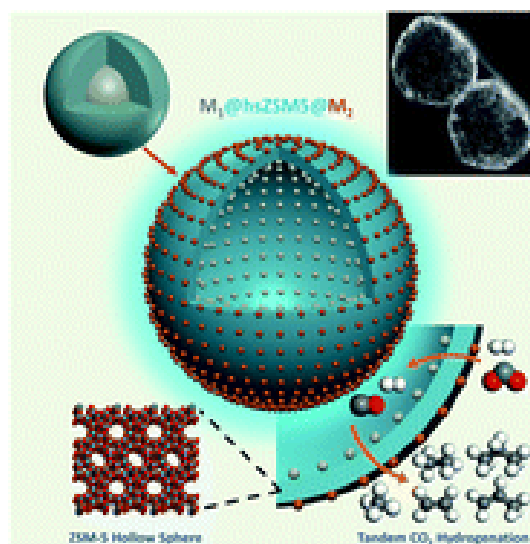
Confirmation of Suzuki–Miyaura cross-coupling reaction mechanism through synthetic architecture of nanocatalysts

Bo Sun, Lulu Ning and Hua Chun Zeng, *Journal of the American Chemical Society*

Abstract: Despite widespread use of heterogeneous Pd catalysts in Suzuki–Miyaura coupling reactions, detailed roles of Pd, especially the nature of its active species, are still a topic of controversial debate. While some studies showed an active surface of Pd nanoparticles or nanoclusters acting heterogeneously, others claimed soluble Pd species leached from the metallic Pd to be active species which are homogeneous in nature. Besides, within the homogeneous mechanism, how the Pd leaches and promotes the cross-coupling reaction is then another question that needs to be addressed. It could be envisioned that if the soluble Pd species and solid-phase Pd are physically separated, the mechanism of Suzuki–Miyaura coupling could then be confirmed through examining the catalytic activity in different reaction regions. Herein we use microporous Stöber silica as a membrane to separate the soluble Pd species from solid Pd and conduct size-selective reactions which allow the passage of leaching Pd species, but not of reactants or products larger than the membrane aperture. With this strategy, we have been able to differentiate the surface reaction from the solution cross-coupling. We find that the leached Pd species are the only genuine catalytic intermediate in the cross-coupling reactions. We also confirm that oxidative addition of aryl halides to the solid Pd leads to leaching of the soluble Pd species which is necessary to promote Suzuki–Miyaura reactions.


A shell-by-shell approach for synthesis of mesoporous multi-shelled hollow MOFs for catalytic applications

Bo Sun and Hua Chun Zeng, *Particle & Particle Systems Characterization*

Abstract: Over the past two decades, advanced materials with hollow interiors have received significant attention in materials research owing to their great application potential across a vast number of technological fields. Though with great difficulty, multi-shelled hollow metal–organic frameworks (MSHMs) have also been successfully synthesized in recent years. Herein, a rational shell-by-shell soft-templating protocol has been devised to fabricate highly uniform multi-shelled hollow cobalt-imidazole-based MOF (ZIF-67). For the first time, it has become possible to endow mesoporosity to this new type of functional material (i.e., mesoporous MOFs). When used as carrier materials in catalytic reactions, in principle, these mesoporous MSHMs with high surface area not only improve the dispersity of metal nanoparticles (NPs), but also efficiently facilitate the mass diffusion of the reactions, resulting in enhanced catalyst activity. Moreover, the obtained MSHMs/M nanocomposites serve as base-metal bifunctional catalysts for one-pot oxidation-Knoevenagel condensation cascade reaction, in which the MSHMs itself serves as a pristine active catalyst in addition to its role of catalyst support. The results demonstrate that excellent multifunctional catalysts can be achieved via preparing intrinsically microporous bulk MOFs into extrinsically mesoporous MSHMs which possess many structural merits that conventional bulk MOFs do not have.
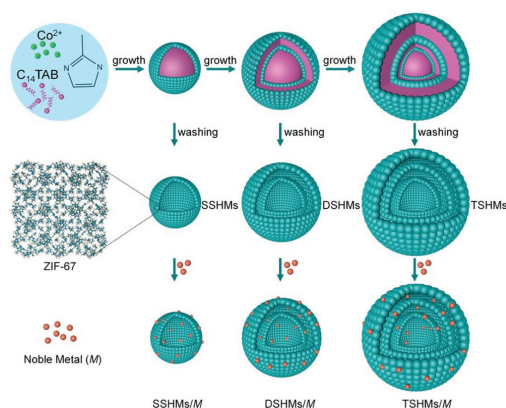
Mesoporous silica encapsulated metal-organic frameworks for heterogeneous catalysis

Hua Chun Zeng, *Matter*

DOI: 10.1016/j.matt.2020.07.013

Abstract: Encapsulation of metal-organic frameworks (MOFs) with a shell of mesoporous silica can boost overall performance of MOFs, offering versatility for synthetic architecture of integrated nanocatalysts with reactor-like features. Recently, Yu et al. report a green approach to make yolk-shell nanoreactors.
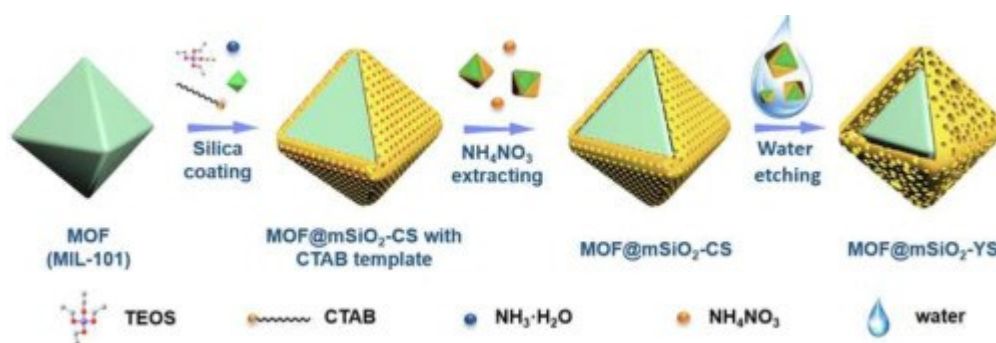
Other activities and achievements

PhD student Perman JORAYEV gave a talk titled 'Multi-objective Bayesian optimisation of a three-step synthesis of terephthalic acid from crude sulphate turpentine' at the *3rd International Conference on Machine Learning and AI in (bio)Chemical Engineering* in Cambridge, UK, 8-9 July.

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 researchers have been focused on the development of the advanced clean synthesis plant for the production of speciality chemicals. Current work has focused on the development of computational algorithms to explore the effects of current distribution and control of the potential distribution in electrosynthetic reactors. Work has continued in collaboration with Dr Dai Chencheng and Dr Zeng Minyu to explore control strategies for the reactor systems under development for nitrogen oxidation. In this process we are exploring a new strategy for nitrate generation which has the potential to offer a significantly lower carbon synthesis route for production of important products such as nitrate. Alongside the electrolyser control aspects experimental studies have focused on promising methods to improve current density. In this area we are employing thin layer synthesis flow cells in conjunction with gas diffusion electrodes (GDEs). In these new structures, the porous diffusion medium of the GDE promotes gas reactant access to the catalyst directly, giving rise to an enhancement of mass transport to develop an optimal product yield.

Electrocatalysis research developments in eCO$_2$RR reactions have been the focus of Dr Sun Libo in the current working period. He is exploring new strategies for single atom catalysts (SACs) applications. In the present work, a ligand composed of 1 10-phenanthroline, namely (Z)-N-(1,10-phenanthrolin-2-yl)-2H-1l2-1,10-phenanthrolin-2-imine (CPYI), was investigated for potential CO$_2$ reduction applications. Metal complexes were prepared with ligands to obtain MCPYI (M = Mn, Fe, Co, Ni and Cu), the Faradaic efficiency was examined for some of these metal complexes, which exhibited considerable FE (above 90%). Then, the partial current density of CO (jCO) for those catalysts were calculated. The work shows when dispersed into molecule catalysts, cobalt-based metal complex always performs the best performance in the application of CO$_2$ reduction.

A programmable electrode-integrated membrane is the focus of a collaboration with Prof. Jim Yang Lee, Dr Zhang Tianran. This activity explores the use of a programmable electrical stimulus which can be used to reduce the frequency of membrane fouling.

The IRP2 start-up company Datum Electronix, launched between Dr Kamal Elouarzaki and Dr Adrian Fisher, has continued to develop new partnerships during the reporting period. Discussions with a Chinese company and a new partner in Malaysia are continuing to develop first-generation water treatment facilities in the mining sector. Collaborations with Prof. Erik Birgersson have expanded through our industrial collaboration with Syngenta. Freyja Dagbjartsdóttir has been working on models to support the intelligent design of next generation electrosynthesis plants. Her work is exploring the effects of local viscosity variation and the influence on current density in an electrochemical synthesis cells where the electrochemical reaction changes the viscosity of the electrolyte. Freyja's new contribution to the field is that the influences are explored systematically and new experiments designed inorder to observe the current density sensitivity predicted due to the viscosity variations.

Dr Adrian Fisher, PI
University of Cambridge

Update on work package 2.1
Advanced electrode architectures

Dr DAI Chencheng (Research Fellow, NTU) has been working on the development of the electrochemical nitrogen oxidation reaction (NOR) in a flow cell employing a gas diffusion electrode (GDE). In the previous work, the electrochemical NOR has been established using spinel oxide catalysts in an H-cell. However, the current density is limited significantly by poor mass transport to the anode due to the low diffusivity and solubility of nitrogen in water. In order to make NOR economically feasible, it is essential to improve the current densities. One of the most promising methods is to use flow cells with GDEs. The porous diffusion medium in the GDE allows the gas reactant to diffuse to the catalyst directly, resulting in enhanced mass transport and improved

current densities. The flow cell was therefore designed and fabricated (shown in the figure below). A series of operational parameters, such as electrolyte/gas flow rate and applied potential, have been tested to obtain the optimal performance. In addition, **Freyja DAGBJARTSDÓTTIR (PhD student, CAM)** has been helping to build up a numerical for the system to better understand the influence of geometrical, operational and physical parameters on the NOR performance. Meanwhile, different methods for nitrate/nitric acid concentration detection (ppm level), including ion chromatography, UV-Vis and ion-selective electrode, have been evaluated for measuring product electrolyte from electrochemical NOR.
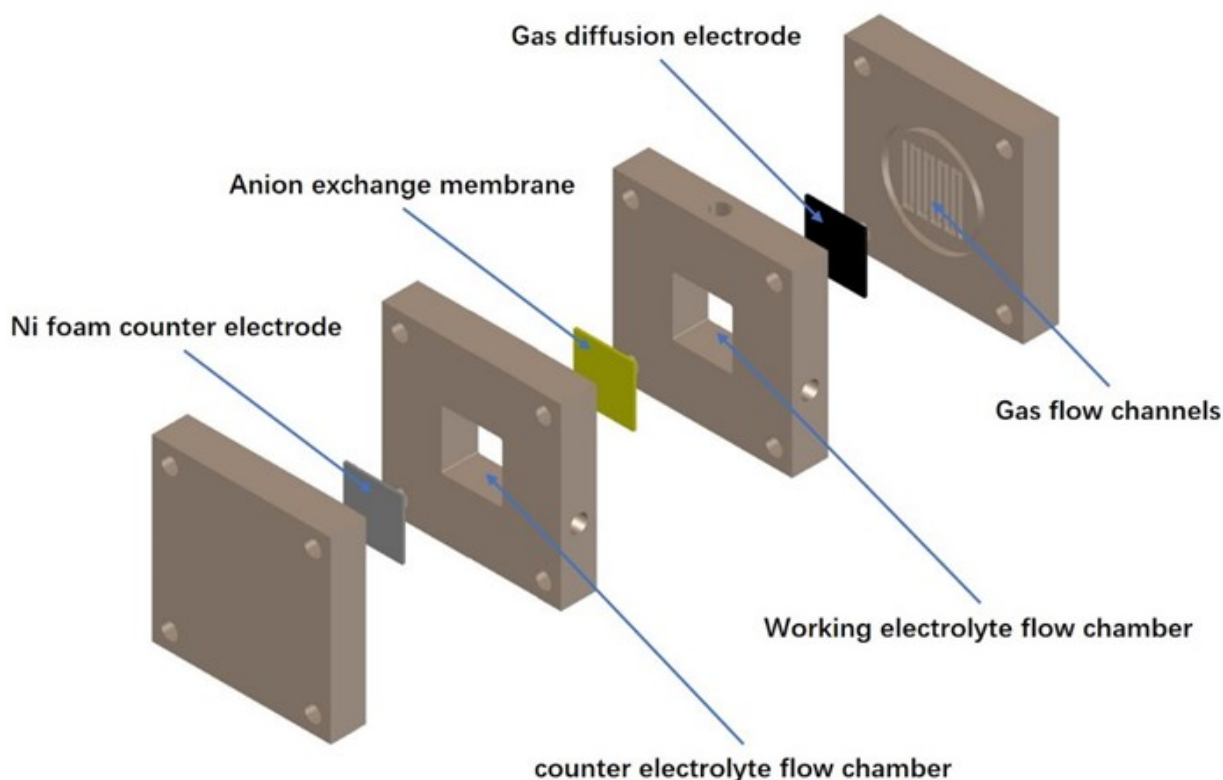

Fig. 2.1: A flow cell that employs a gas diffusion electrode for improved performance.

Dr DAI Chencheng

Nur Farhanah BTE ROSLI's (PhD student, NTU) recent work explored pnictogens, specifically arsenic, as nanomachines for biomedical applications. Thus far, diverse types of materials have been explored as nanomachines for biomedical applications but pnictogen nanomachines are still in their infancy. Analogous to graphene, pnictogens are Group V elemental nanomaterials, specifically arsenic, antimony and bismuth, with semiconducting electronic properties and which have shown potential in various applications.

Template-less arsenene-based Janus nanomachines with layered structures were modified with platinum, forming As-Pt nanomotors. Thereafter, their motion capabilities, biocompatibility and drug loading competency were thoroughly investigated. The results showed fast, biocompatible, high drug loading and high cellular uptake of As-Pt nanomotors. These findings open new direction in arsenene nanoparticles as non-toxic self-propelled drug carrier applications.
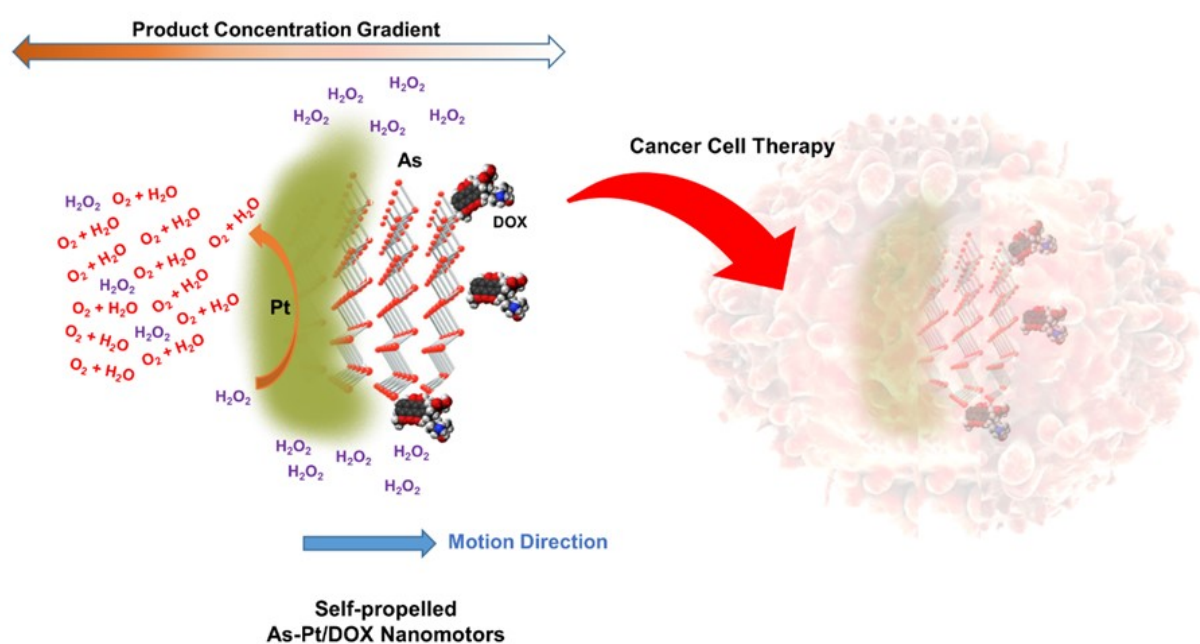

Fig. 2.2: Use of nanomachines for cancer cell therapy.

Nur Farhanah BTE ROSLI

THAM Guo Xiong's (PhD student, NTU) main research interest lies in the study of electrochemical processes and the development of its relevant applications such as sensors and electrochemical energy storage. Recently, he has successfully defended his doctoral thesis titled 'Electrochemistry of Thin Film Electrodes via Surface Modification'.

At the same time, he submitted a scientific publication that was accepted and approved for publication. The publication is titled 'Voltammetric studies on surface-modified electrodes with functionalised carbon nanotubes under different dispersion conditions' and has been published in the journal *Electrochimica Acta*.
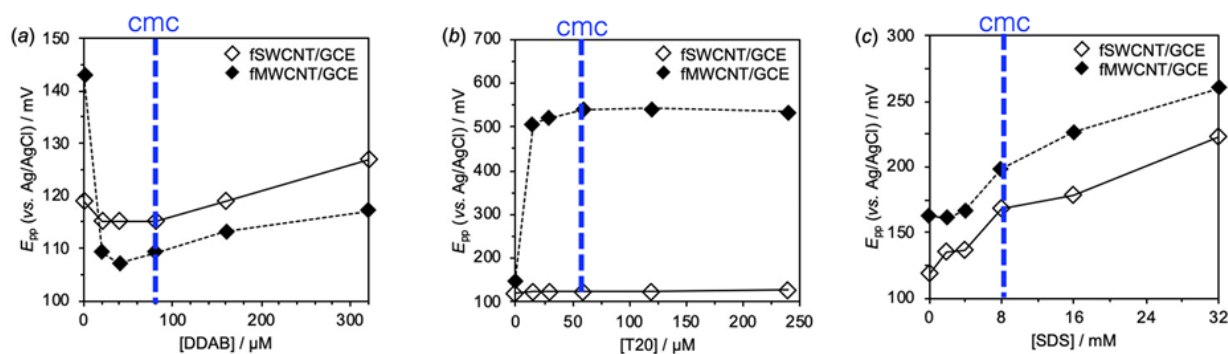
Fig. 2.3: Examining the effect of varying surfactant concentration on peak-to-peak potential separation (ΔEpp): The smallest change in ΔEpp was observed with before and after addition of (a) DDAB into the bulk solution with the immersed fCNT/GCE film electrode than with (b) T20 and (c) SDS into bulk solution.

THAM Guo Xiong

Update on work package 2.2
Co-generation and electrolytic synthesis reactor engineering

In **Dr SUN Libo's (Research Fellow, NTU)** previous work, a new N4-conjugated macrocyclic ligand based on 1 10-phenanthroline subunit was used to prepare the CoiiCPY metal complex, which exhibited high selectivity and activity for CO_2 reduction to CO. In the present work, another similar ligand composed of 1 10-phenanthroline, namely (Z)-N-(1,10-phenanthrolin-2-yl)-2H-1l2-1,10-phenanthrolin-2-imine (CPYI), is proposed for CO_2 reduction research. A series of metal complexes were prepared with such ligands to obtain MCPYI (M = Mn, Fe, Co, Ni and Cu). As shown in the figure, from the Faradaic efficiency calculation towards CO, both the metal complexes of CoCPYI, MnCPYI and NiCPYI exhibited considerable FE (above 90%) from -1.2 to -1.3 V vs. Ag/AgCl, while that of FeCPYI and CuCPYI just decrease with potential applied. Then, the partial current density of CO (jCO) for those catalysts were calculated. However, the jCO tested for MnCPYI, FeCPYI and CuCPYI were rather low, while that of CoCPYI is the highest, and that of NiCPYI ranked second. The work proved that when dispersed into molecule catalysts, cobalt-based metal complex always performs the best performance in the application of CO_2 reduction.
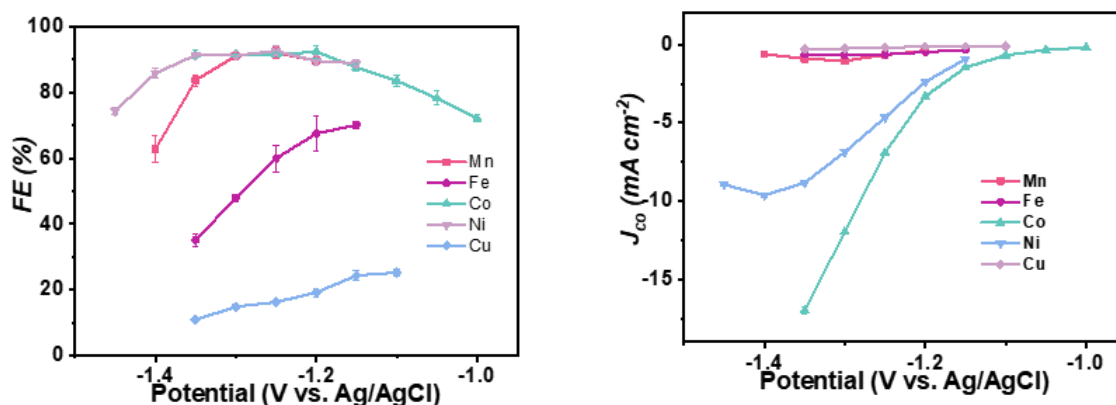

Fig. 2.4: (left) Faradaic efficiency of CO. (right) Partial current density of CO.

Dr SUN Libo

Dr ZHANG Shengliang (Research Fellow, NUS) has been working on dual-band electrochromic smart windows capable of independent control of near-infrared (NIR) and visible (VIS) light transmittance. His most recent work was focused on using plasmonic oxygen deficient TiO_{2-x} nanocrystals (NCs) for dual-band electrochromic smart windows with efficient energy recycling. It is found that oxygen deficient TiO_{2-x} NCs is an effective single-component dual-band electrochromic material, and that oxygen vacancy creation is more effective than aliovalent substitutional doping to introduce dual-band properties to TiO_2 NCs. Oxygen vacancies not only confer good NIR-selective modulation, but also improve the Li^+ diffusion in the TiO_{2-x} host, circumventing the disadvantage of aliovalent substitutional doping with ion diffusion. Consequently optimised TiO_{2-x} NC films are able to modulate the NIR and VIS light transmittance independently and effectively in three distinct modes with high optical modulation (95.5% at 633 nm and 90.5% at 1200 nm), fast switching speed, high bistability and long cycle life. An impressive dual-band electrochromic performance was also demonstrated in prototype devices. The use of TiO_{2-x} NCs enables the assembled windows to recycle a large fraction of energy consumed in the colouration process ("energy recycling") to reduce the energy consumption in a round-trip electrochromic operation.
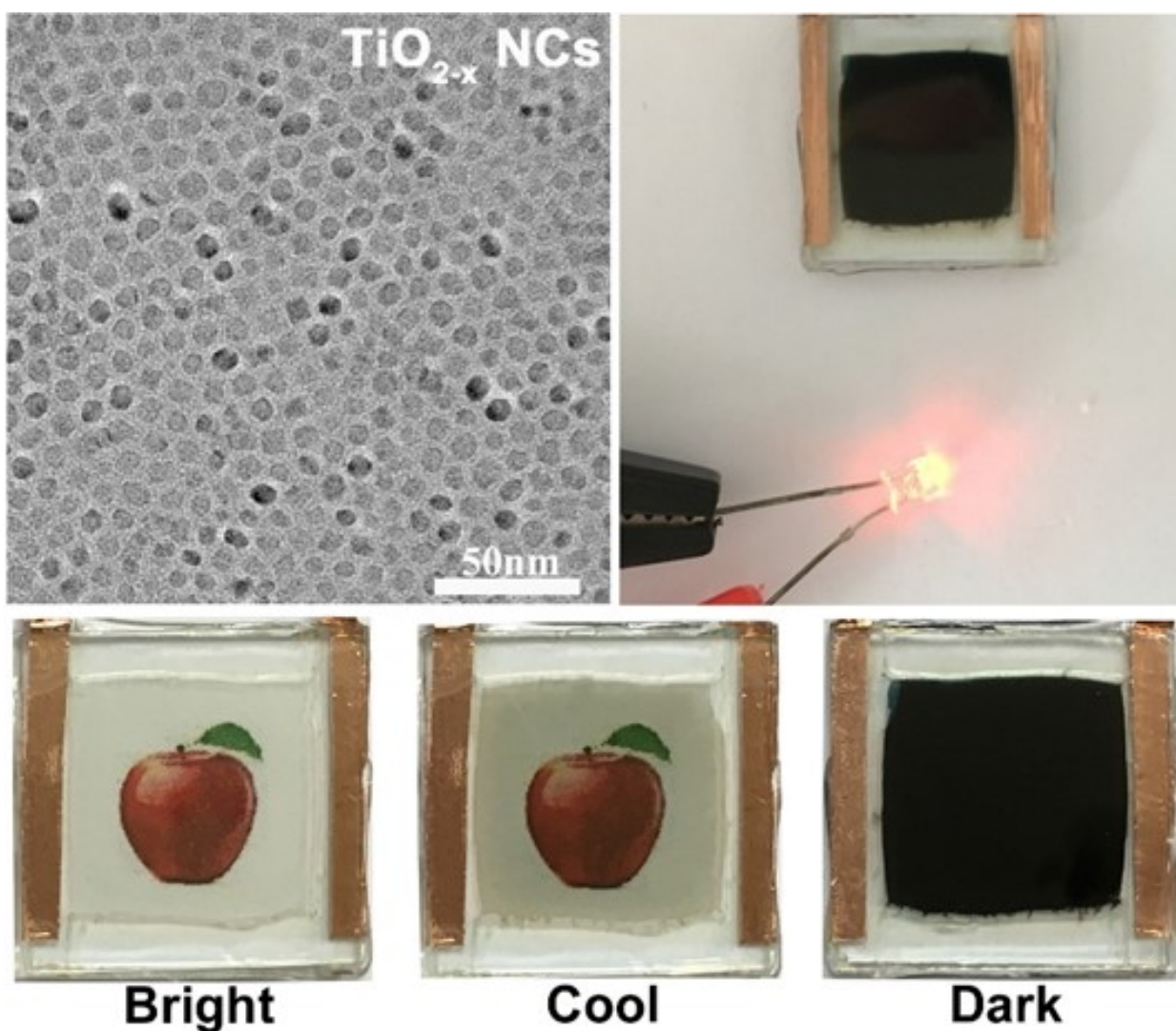

Fig. 2.5: The TEM image of the TiO_2 NCs, and the digital photos of the assembled windows in different operating modes.

Dr ZHANG Shengliang

Dr ZHANG Tianran (Research Fellow, NUS) reports that the incompatibility of bifunctional catalysts is an important issue for rechargeable metal-air batteries that limits the cyclic lifetime of the batteries. The high voltage of charge process (usually > 2 V) unavoidably induces surface oxidation of the catalysts, which is not harmful to OER activities of catalysts but fatal to their ORR activities (Figure 2.6a). To overcome the problem, Dr Zhang Tianran designed a smart air electrode architecture by using a sulfuno-polyaniline (SPANI) layer to protect the bifunctional catalyst. The SPANI layer is highly conductive in the discharge voltage range but turns to low conductivity at high voltage of charging process. This potential-dependent electronic property is used to protect the electro-oxidation of ORR active sites of bifunctional catalyst during the charge process and preserves its activity during discharge (Figure 2.6b). With this smart air electrode design and a noble-metal like ZnCo-P/NC bifunctional catalyst, the rechargeable Zn-air battery with a quasi-neutral $NH_4Cl-ZnCl_2$ electrolyte can deliver a durable cyclic performance with limited increase of the voltage gap, which is more stable than the regular quasi-neutral Zn-air battery Figure 2.6c).
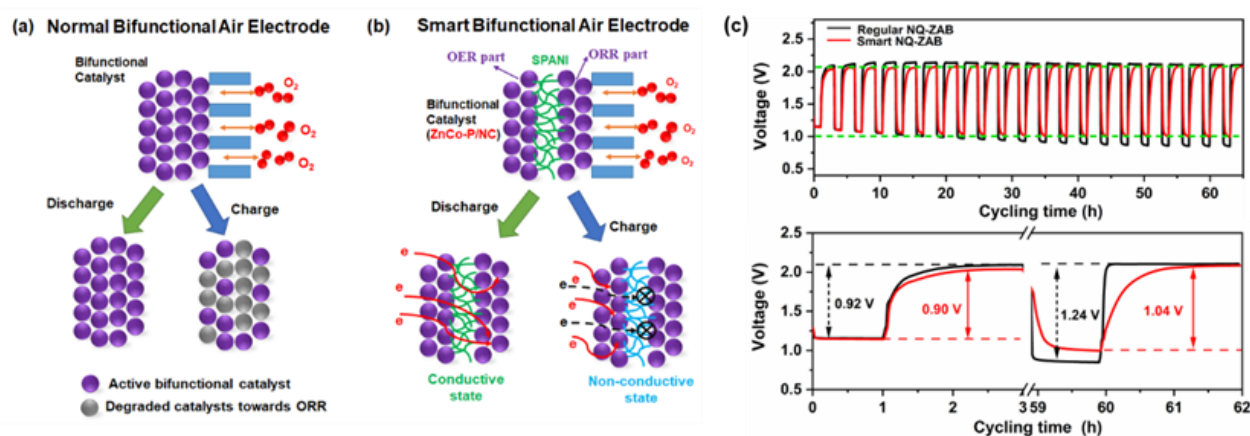

Fig. 2.6: The diagram of (a) regular air electrode and (b) the "smart" air electrode for quasi-neutral zinc air batteries. (c) The cyclic stabilities of the smart quasi-neutral zinc air battery, comparing with a regular quasi-neutral zinc air battery.

Dr ZHANG Tianran

Update on work package 2.3
Micro-variable pressure and temperature electrosynthesis plant

Freyja Björk DAGBJARTSDÓTTIR'S (PhD student, CAM) research interests lie in investigating novel electrochemical systems and the design of advanced electrochemical synthesis plants, where a complex relationship exists between chemistry and mass transport. The aim is to develop numerical and analytical descriptions of electrochemical systems that can be used to investigate, design and monitor these systems. Freyja Dagbjartsdóttir has been working on models describing the influence a local viscosity change has on current density in an electrochemical channel flow cell where the electrochemical reaction changes the viscosity of the electrolyte. A viscosity change that can be caused by, for example, a change in pH or cross-link formation in polymer solutions, can influence multiple aspects of the mass transfer within the cell. This affects the current density and/or Faradaic efficiency. Freyja Dagbjartsdóttir decouples these different influences and investigates one effect at a time to gain a deeper understanding of how a change in viscosity influences reactors. She has also recently started building a numerical model for a nitrate flow reactor. Dr Chencheng Dai has built a prototype flow cell reactor and the idea is for the numerical model to aid in understanding the effects of different geometrical, operational and physical parameters and uncertainties on the current densities and Faradaic efficiency. Freyja Dagbjartsdóttir's PhD is jointly funded by CARES and Syngenta.

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 17.

Quantifying Operating Uncertainties of a PEMFC – Monte Carlo-Machine Learning Based Approach

Kannan, Vishvak, Hansong Xue, K. Ashoke Raman, Jiasheng Chen, Adrian Fisher, and Erik Birgersson, *Renewable Energy*

Abstract: To enhance efficiency, maintain performance and prolong the lifetime of a PEMFC functioning under diverse operating conditions, development of robust control strategies, which encompasses not only the ohmic loss region but also the activation and concentration loss regions, is indispensable. However, a reliable control strategy can be developed only with the information on the uncertainties in extrinsic and intrinsic input parameters in all the three regions of operation. To achieve this, we perform Monte Carlo simulation to correlate the simultaneous variation of 33 input parameters to the cell performance, water, and thermal management in all three regions of operation. Then, the critical parameters in each region of operation are ranked using sensitivity analysis. The catalyst parameters and operating cell potential have a significant influence in activation loss and ohmic loss regions, while the operating pressure and physical parameters affect the concentration loss region significantly. Subsequently, based on these sensitivities we develop reduced regression models to predict the cell performance, without having to solve the full set of equations, with at least 90% accuracy using machine learning techniques. Finally, we also statistically discuss the distribution of cell performance in all three regions of operation.
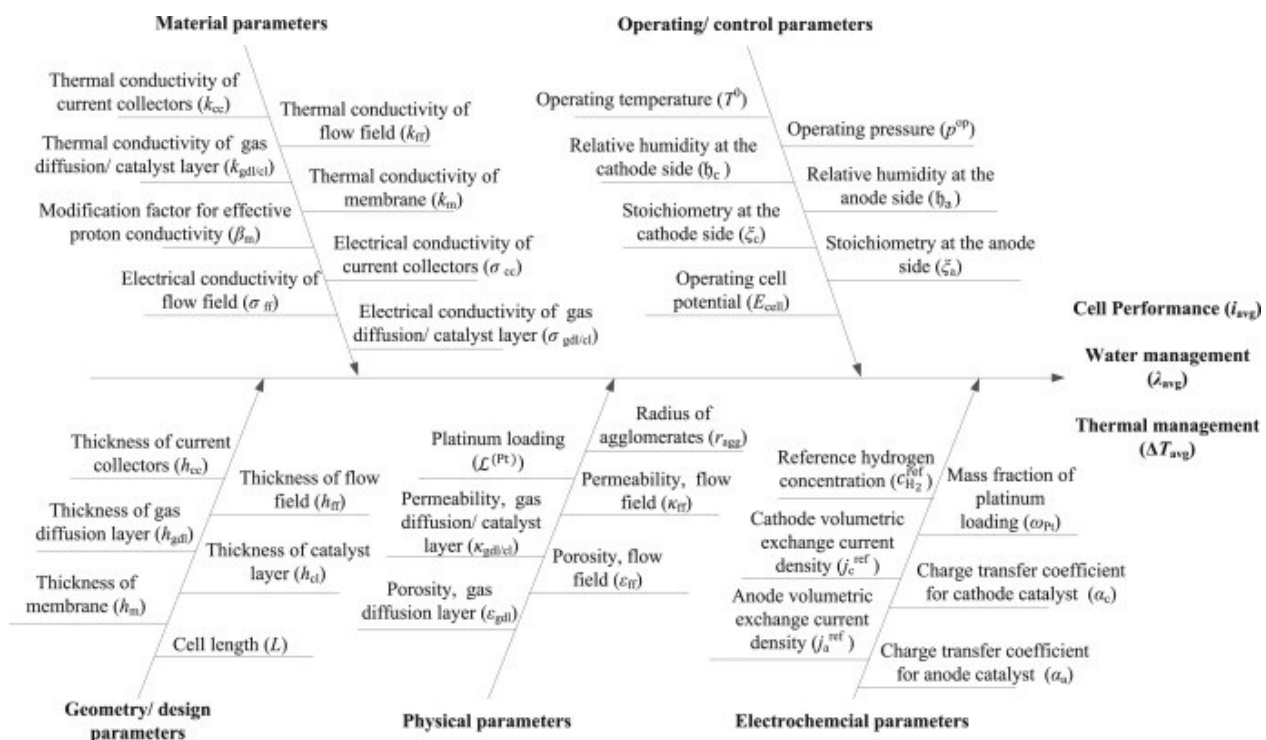
Cause and effect "fish-bone" diagram relating the effects of input parameters to the cell performance, water and thermal management of the PEMFC.

A multi-walled carbon nanotubes coated 3D printed anode developed for biophotovotaic applications

Aazraa O. Pankan, Kamran Yunus, Ela Sachyani, Kamal Elouarzaki, Shlomo Magdassi, Minyu Zeng, and Adrian C. Fisher, *Journal of Electroanalytical Chemistry*

Abstract: We report a method for the design and fabrication of 3D printed bioanodes for Biophotovotaic (BPV) applications. Electrodes were fabricated in 5 different thicknesses, from 0.2 mm to 1.0 mm with a 0.2 mm increment and the electrodes were coated with multi-wall carbon nanotubes (MWCNTs). Electrochemical characterisation of these electrodes was performed and the performance tested alongside a bare carbon paper electrode in a bespoke designed membrane electrode assembly (MEA)-type BPV device.

All of the MWCNTs-coated 3D printed electrodes outperformed the bare carbon paper electrode. The best performing one (1.0 mm) showed a 40 times increment in power density and a 20 times reduction of the internal resistance. The successful development of the 3D printed bioanode can be used as a standardised platform for the comparison of similar materials. The development of the electrodes and MEA-type BPV device will serve as the initial step towards the development of a monolithic 3D printed BPV platform.
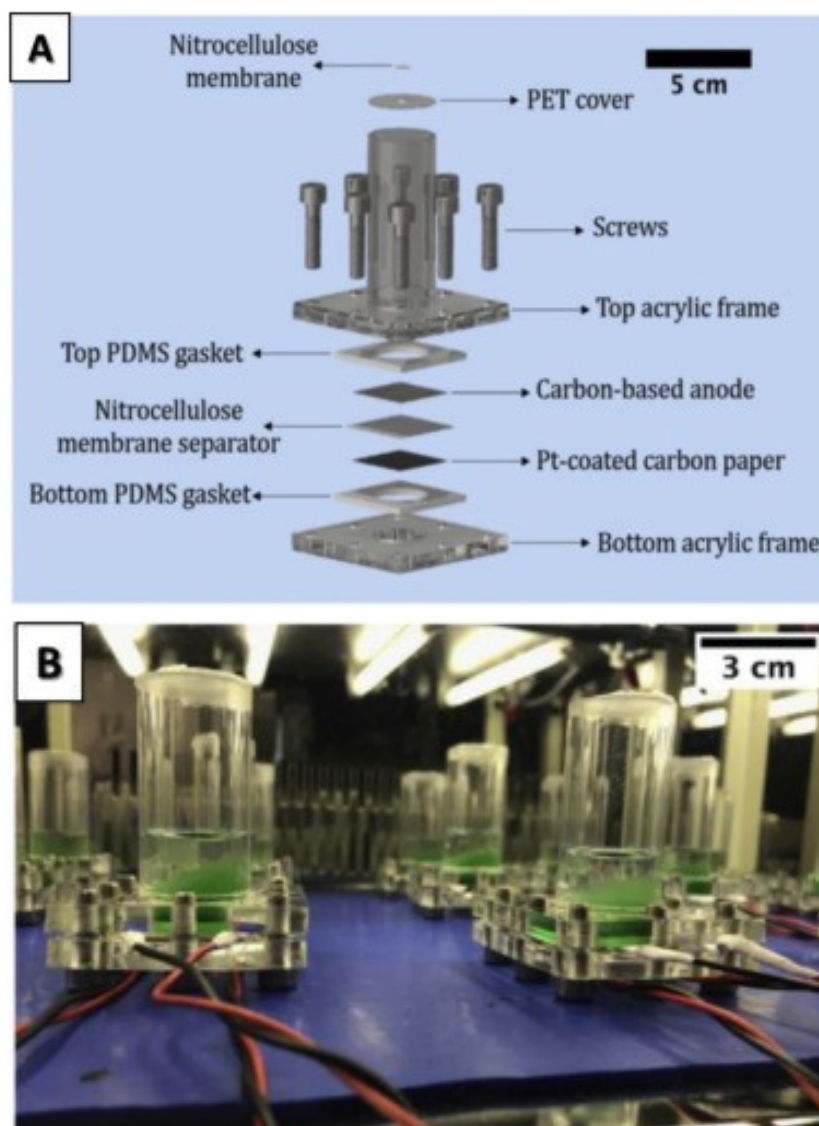

Illustration of the special designed MEA-type BPV device (a) a schematic diagram and (b) actual devices inoculated with cultures of S. elongatus.

Constructing an adaptive heterojunction as a highly active catalyst for the oxygen evolution reaction

Xiao Ren, Chao Wei, Yuanmiao Sun, Xiaozhi Liu, Fanqi Meng, Xiaoxia Meng, Shengnan Sun, Shibo Xi, Yonghua Du, Zhuanfang Bi, Guangyi Shang, Adrian C. Fisher, Lin Gu and Zhichuan J. Xu, *Advanced Materials*

Abstract: Electrochemical water splitting is of prime importance to green energy technology. Particularly, the reaction at the anode side, namely the oxygen evolution reaction (OER), requires a high overpotential associated with $O-O$ bond formation, which dominates the energy-efficiency of the whole process. Activating the anionic redox chemistry of oxygen in metal oxides, which involves the formation of superoxo/peroxo-like $(O_2)_n^-$, commonly occurs in most highly active catalysts during the OER process. In this study, a highly active catalyst is designed: electrochemically delithiated $LiNiO_2$, which facilitates the formation of superoxo/peroxo-like $(O_2)_n^-$ species, i.e., NiOO*, for enhancing OER activity. The OER-induced surface reconstruction builds an adaptive heterojunction, where NiOOH grows on delithiated $LiNiO_2$ (delithiated-$LiNiO_2$/NiOOH). At this junction, the lithium vacancies within the delithiated $LiNiO_2$ optimize the electronic structure of the surface NiOOH to form stable NiOO* species, which enables better OER activity. This finding provides new insight for designing highly active catalysts with stable superoxo-like/peroxo-like $(O_2)_n^-$ for water oxidation.
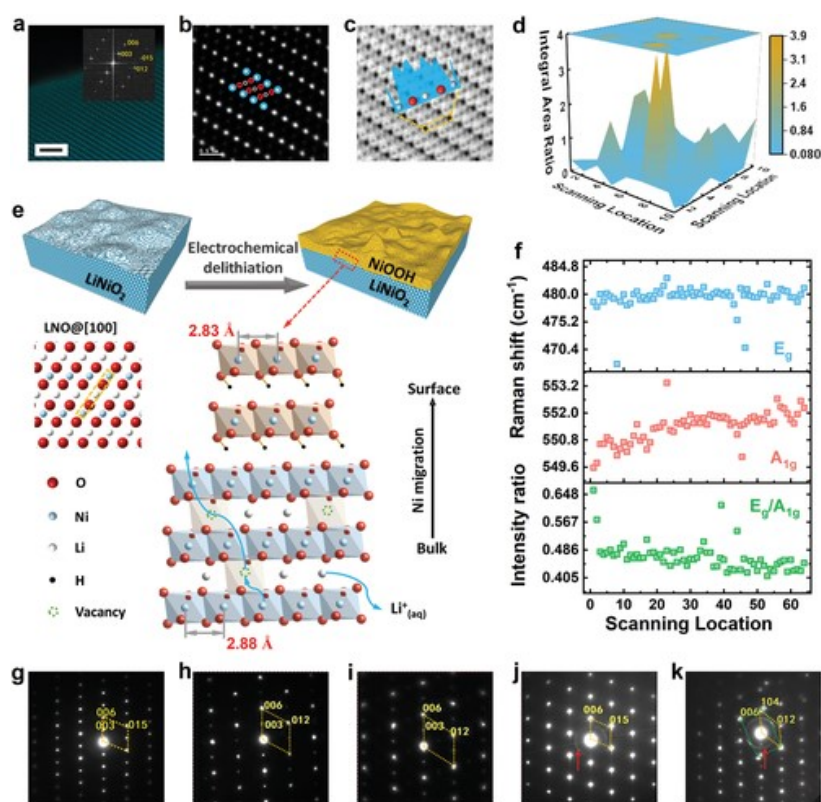
(a) High-resolution HAADF-STEM image of pristine $LiNiO_2$. The corresponding FFT pattern indexed to R-3m space group is shown in inset of (a). Scale bar, 2 nm. (b, c) Atomic resolution HAADF-STEM image of pristine LiNiO2, the insets shows a typical image of the unit cell and its pseudocolor representation. Individual columns of Ni atoms are clearly recognized. The corresponding ABF with the line profile acquired at the orange dashed line rectangular zone shown in (c). (d) 12 μm × 12 μm Raman mapping image of LNO-500. The image was collected at 1.5 μm resolution. The intensities of blue and orange correspond to the integral area ratio of the $LiNiO_2$ and NiOOH. (e) The schematic diagram of the evolution of $LiNiO_2$ in electrochemical process. (f) Fitted Raman frequency position and band intensities ratio of the Eg and A1g Raman modes at different scanning locations. (g–k) Selected-area electron diffraction (SAED) images along the [100] zone axis of the space group R-3m of $LiNiO_2$. The SAED patterns are of: (g) LNO-0, (h) LNO-KOH, (i) LNO-50, (j) LNO-500 and (k) LNO-1000.

Covalency competition dominates the water oxidation structure–activity relationship on spinel oxides

Yuanmiao Sun, Hanbin Liao, Jiarui Wang, Bo Chen, Shengnan Sun, Samuel Jun Hoong Ong, Shibo Xi, Caozheng Diao, Yonghua Du, Jia-Ou Wang, Mark B. H. Breese, Shuzhou Li, Hua Zhang and Zhichuan J. Xu, *Nature Catalysis*

Abstract: Spinel oxides have attracted growing interest over the years for catalysing the oxygen evolution reaction (OER) due to their efficiency and cost-effectiveness, but fundamental understanding of their structure–property relationships remains elusive. Here we demonstrate that the OER activity on spinel oxides is intrinsically dominated by the covalency competition between tetrahedral and octahedral sites. The competition fabricates an asymmetric MT–O–MO backbone where the bond with weaker metal–oxygen covalency determines the exposure of cation sites and therefore the activity. Driven by this finding, a dataset with more than 300 spinel oxides is computed and used to train a machine-learning model for screening the covalency competition in spinel oxides, with a mean absolute error of 0.05 eV. [Mn]T[Al0.5Mn1.5]OO4 is predicted to be a highly active OER catalyst and subsequent experimental results confirm its superior activity. This work sets mechanistic principles of spinel oxides for water oxidation, which may be extendable to other applications.
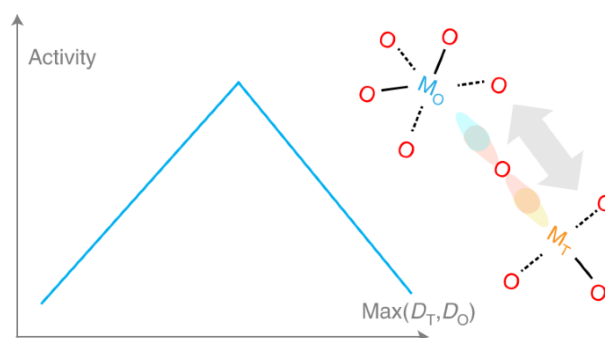

Spin-Related Electron Transfer and Orbital Interactions in Oxygen Electrocatalysis

Yuanmiao Sun, Shengnan Sun, Haitao Yang, Shibo Xi, Jose Gracia and Zhichuan J. Xu, *Advanced Materials*

Abstract: Oxygen evolution and reduction reactions play a critical role in determining the efficiency of the water cycling (H2O ⇔ H2 + 1/2O2), in which the hydrogen serves as the energy carrier. That calls for a comprehensive understanding of oxygen electrocatalysis for efficient catalyst design. Current opinions on oxygen electrocatalysis have been focused on the thermodynamics of the reactant/intermediate adsorption on the catalysts. Because the oxygen molecule is paramagnetic, its production from or its reduction to diamagnetic hydroxide/water involves spin-related electron transfer. Both electron transfer and orbital interactions between the catalyst and the reactant/intermediate show spin-dependent character, making the reaction kinetics and thermodynamics sensitive to the spin configurations. Herein, a brief introduction on the spintronic explanation of the catalytic phenomena on oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) is given. The local spin configurations and orbital interactions in the benchmark transition-metal-based catalysts for OER and ORR are analyzed as examples. To further understand the spintronic oxygen electrocatalysis and to develop more efficient spintronic catalysts, the challenges are summarized and future opportunities proposed. Spin electrocatalysis may emerge as an important topic in the near future and help integrate a comprehensive understanding of oxygen electrocatalysis.
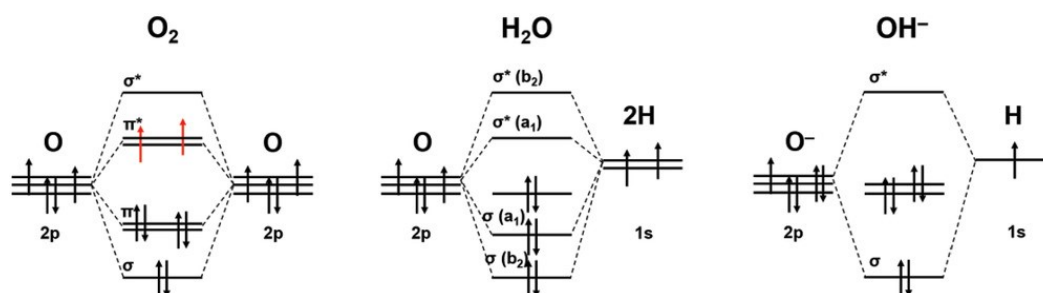
Voltammetric studies on surface-modified electrodes with functionalised carbon nanotubes under different dispersion conditions

Guo Xiong Tham, Adrian C. Fisher and Richard D. Webster *Electrochimica Acta*

Abstract: Quantitative analysis was performed on voltammetric data obtained from surface-modified electrodes that were prepared with functionalised carbon nanotubes (fCNTs) consisting of functionalised single-walled carbon nanotubes (fSWCNTs) and functionalised multi-walled carbon nanotubes (fMWCNTs). In order to obtain the optimum coating procedure, the fCNTs were dispersed in individual solutions of N-methyl-2-pyrrolidone, N,N-dimethylformamide and ethanol (EtOH), and drop cast onto glassy carbon (GC) electrode surfaces to become the surface-modified electrodes. Different classes of surfactants (positive, negative and neutrally charged) at varying concentrations were tested in the bulk solution to see how they affected the dispersion properties of the fCNTs as well as how they influenced the experimental heterogeneous electron transfer rates (k0) measured via cyclic voltammograms (CVs) of the ferri-/ferrocyanide redox couple at the immersed film electrodes. The k0-values measured at the fSWCNT/GCE and fMWCNT/GCE film electrodes were compared and the results indicated that the type of fCNTs and the %wt of the fCNTs used in the dispersion did not affect the rates of heterogeneous electron transfer. The effect of increasing bulk surfactant concentration was examined to determine the optimum current responses with the lowest voltammetric peak-to-peak separation (ΔE_{pp}) values for the film electrodes. Thin layer diffusion and semi-infinite diffusion processes were found to be dominant at slow and fast scan rates, respectively.
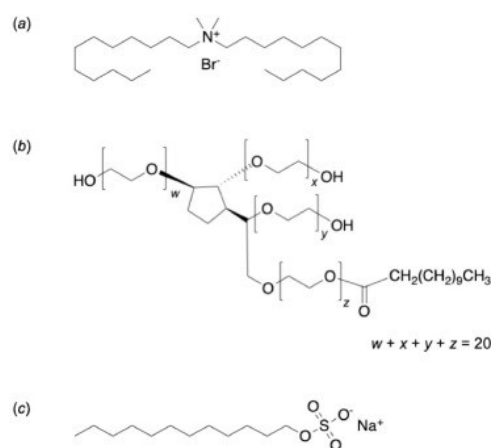
Chemical structures of (a) DDAB, (b) T20, and (c) SDS.

Ir-Skinned Ir-Cu Nanoparticles with Enhanced Activity for Oxygen Reduction Reaction

Jiarui Wang, Ye Zhou, Libo Sun, Jingjie Ge, Jingxian Wang, Chencheng Dai and Zhichuan Xu, *Chemical Research in Chinese Universities*

Abstract: The development of methanol-tolerate oxygen reduction reaction(ORR) electrocatalysts is of special significance to direct methanol fuel cells system. Iridium is known for its better methanol tolerance than platinum and able to survive in harsh acidic environment. However, its activity is relatively low and thus the approach to improve Ir's ORR is desired. Herein, bimetallic Ir-Cu nanoparticles(NPs) with controllable Ir/Cu compositions(ca. 1:2 to 4:1, atomic ratio) are synthesized via a galvanic replacement-based chemical method. The as-synthesized Ir-Cu NPs are investigated as ORR catalysts after electrochemically leaching out the surface Cu and forming Ir-skinned structures. Around 2- to 3-fold enhancement in the intrinsic activity has been observed in these Ir-skinned Ir-Cu catalysts compared to Ir counterpart. The approach is demonstrated to be a promising way to prepare efficient Ir ORR catalysts and lower catalyst cost.

Other activities and achievements

PhD student THAM Guo Xiong presented a poster titled 'Voltammetric studies on surface-modified electrodes with functionalised carbon nanotubes under different dispersion conditions' at the 3rd *Chemistry National Meeting Singapore (ChnmSG-3)* from 9-10 September 2020.

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 spite of the much reduced laboratory activity due to the pandemic, during this reporting period we have been able to put our recently commissioned particle characterisation equipment to good use. This includes in particular a new air quality measurement device that we have applied to ascertain the concentrations of various pollutants, which include apart from particulate matter also nitric and sulfur oxides, along the coastline of Singapore. Such measurements provide a natural tie-in with the J-Park Simulator, which we use to simulate exactly those emissions from ships – a topic of particular relevance to Singapore.

In terms of modelling, we have continued to invest much of our efforts into investigating potential ways how polycyclic aromatic hydrocarbons (PAHs) – the main constituents of soot – can stick together at flame conditions in order to form the first, incipient soot particles. This question remains at the heart of soot research, being one of its main unresolved puzzles. By means of molecular dynamics simulations, we have found that PAHs in soot particles must be connected with cross-links between them in order for the particles to exhibit the same mechanical properties as observed through nanoindentation experiments. Furthermore, using first-principles quantum chemistry calculations, we have studied localised π-radical PAHs. These compounds appear to be present in significant concentrations at flame temperatures and have been found to form strongly bound stacks, thus indicating that they may play an important role in soot formation. The results of our computations on the kinetics of some reactions involving this type of PAHs suggest that these reactions may be even faster than some of the processes that form cross-links. In addition, we found substantial equilibrium constants for these reactions, which implies that they are likely to be strongly favoured at flame temperatures.

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

Dr ZONG Yichen (Research Fellow, NUS) has been leading the experimental research on future fuels for low-emission energy conversion. The research activities are conducted primarily through the collaboration of NUS and Cambridge researchers. Since the lab has reopened following closure due to the pandemic, a series of engine experiments has been performed using diesel, jet fuel, marine oil and a PODE additive. The combustion efficiency and soot emission are two key indicators under investigation. In the experiments, a DMS particle sizer is used to obtain the size distribution and number concentration of the particulates and a Soot Particle Aerosol Mass Spectrometer (SP-AMS) is used to obtain the chemical composition of the emission. Dr Zong Yichen also started a new measurement campaign at the coastline of Singapore using AQ-Mesh monitor. The ambient PM, NO_x, SO_2, CO, O_3 and CO_2 concentrations are recorded and transmitted to the J-Park Simulator (JPS) to study the impact of shipping emissions.

TAN Yong Ren (PhD student, CAM) has recently published his work titled 'The effect of poly (oxymethylene) dimethyl ethers ($PODE_3$) on soot formation in ethylene/$PODE_3$ laminar coflow diffusion flames' in *Fuel*. He is currently investigating the structural effects of C3 oxygenated fuels on soot formation in ethylene coflow diffusion flames. The selected C3 oxygenated fuels are dimethyl carbonate (DMC), dimethoxymethane (DMM) and isopropanol (IPA). They were studied due to their practical value as fuel additives in engines. He has doped the fuels with ethylene at 5% in flame and measured the particle size distribution (PSD) at the centre-line of the flames to understand the particle evolution changes due to the blending of the C3 oxygenated fuels in ethylene. From Figure 3.2, following the PSDs from low non-dimensional axial position (NDAP) to high NDAPs, the blended and non-blended fuels exhibited transition from unimodal PSDs to bimodal PSDs. This suggests that they undergo a similar transition in PSDs with increasing NDAP.
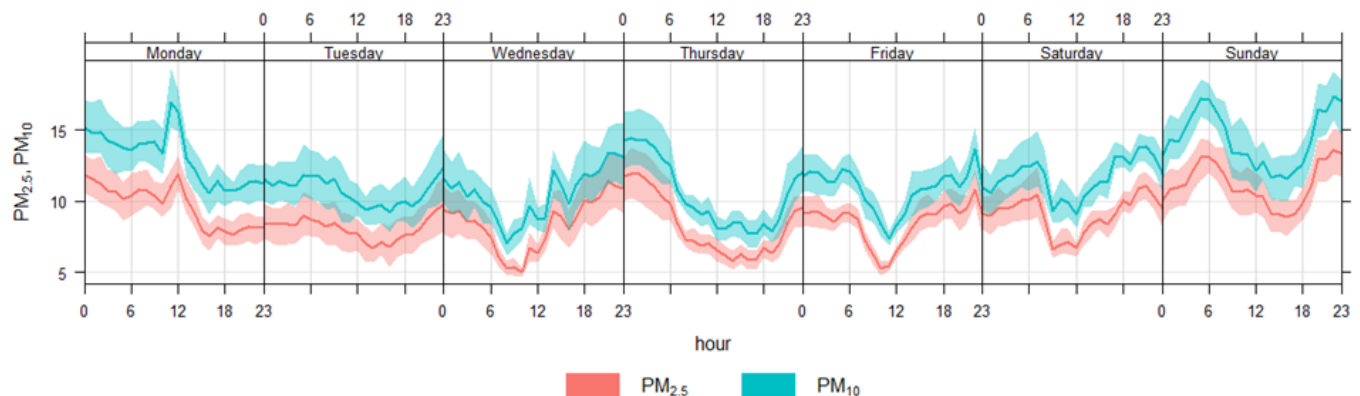

Fig 3.1: Weekly PM record at Singapore coastline.

Dr ZONG Yichen

Additionally, from Figure 3.2c, the broadened uni-modal PSDs (to larger particle sizes) for the doped flames also suggests that there is faster growth of particles in the flames.
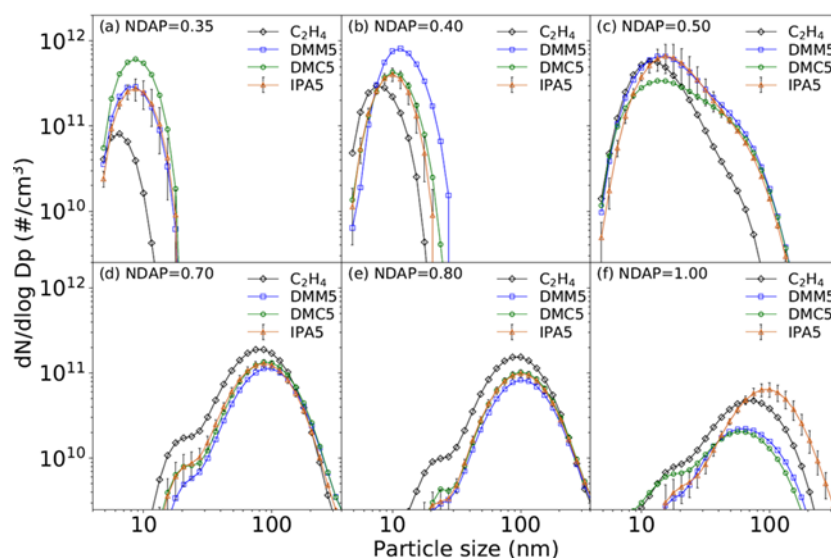

Fig. 3.2: Particle size distributions measured along the centre-line of C_2H_4 (ethylene), DMC5 (5% blend of DMC), DMM5 (5% blend of DMM) and IPA5 (5% blend of IPA) flames. The data are grouped by non-dimensional axial position (NDAP) (a) NDAP=0.35, (b) NDAP=0.40, (c) NDAP=0.50, (d) NDAP=0.70, (e) NDAP=0.80 and (f) NDAP=1.00. The error bars show the standard error of the measurements at each position over four repeats.

TAN Yong Ren

Clifford VO Chi Hung (PhD student, NUS) main research interest lies in the biological fixation of CO_2 using the archaeon *M. maripaludis* S2. Unlike many other microbes which require organic feedstock, this microorganism can convert CO_2 into CH_4 without any organic carbon input. While studying this methanogen, he has discovered a metabolic adaptation called an acetate switch, which has not been reported in autotrophs before. He has reported his finding in a publication, 'First observation of an acetate switch in a methanogenic autotroph (*Methanococcus maripaludis* S2)' in *Microbiology Insights*. Clifford Vo Chi Hung is planning for the last experiment on flux measurements of *M. maripaludis* S2 grown in formate and writing his thesis.
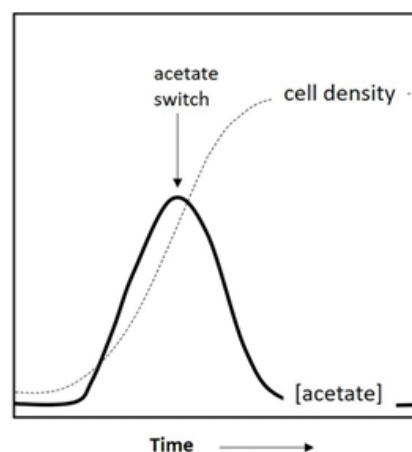

Fig. 3.3: A schematic of acetate switch profile. Acetate concentration increases to a maximum in the early growth phase and decreases thereafter. Acetate concentration reaches zero as the cells enter the stationary phase.

Clifford VO Chi Hung

Update on work package 3.2

Refinery, fuel and engine of the future — modelling
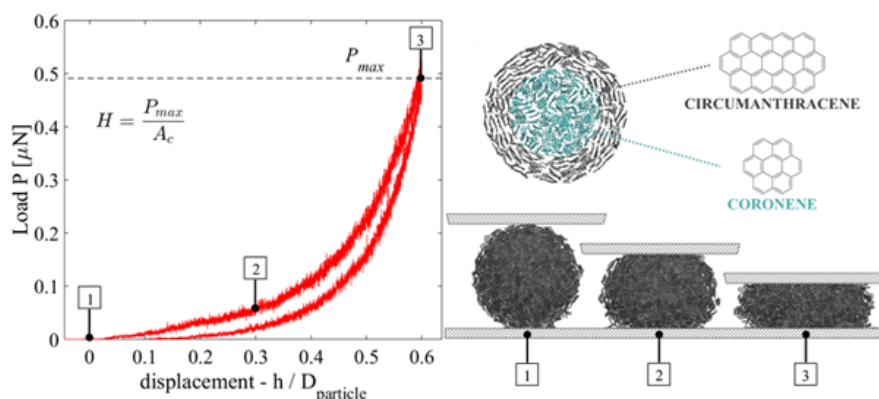*Chemical mechanisms, PAH chemistry, after-treatment*

Fig. 3.4: Exploring the internal structure of soot particles using nanoindentation: a reactive molecular dynamics study.

Dr Laura Pascazio

Laura PASCAZIO's (Research Fellow, CAM) main research interest lies in the study of combustion-generated carbonaceous nanoparticle (also known as soot) formation using computational methods. The understanding of the soot inception mechanism remains one of the most debated topics in the combustion scientific community. Recently, she has been focusing on crosslinking reactions that may lead to particle formation at high temperatures. She has recently published a paper in which she developed a new soot model in which soot precursors (polycyclic aromatic hydrocarbons) are crosslinked in a 3D network. The paper shows that soot particles must present crosslinks between their constituents to have the same mechanical properties found experimentally. Jointly with **Dr Jacob MARTIN**, she is now preparing a paper on the importance of localised π-radicals in soot formation. These compounds were found to form strongly bound stacked complexes indicating a potentially important role in soot formation.

Dr Jacob MARTIN (Research Fellow, CAM) has been continuing to explore the formation of the pollutant soot in flames, as well as the nanostructure of carbon materials. In carbon materials science, Dr Jacob Martin has been exploring the self-assembly of curved aromatic species with colleague Kimberly BOWAL. They have shown that curvature does not impact the core-shell structure previously seen for flat PAHs but it does disrupt the alignment of molecules that is critical for graphitisation of carbon materials. Ions are seen to stabilise small clusters of curved PAHs, but not nanoscale clusters, and mixing is not possible between curved and planar structure. This work also developed the curPAHIP forcefield for larger PAHs, which is important for considering flexoelectric effects in carbon materials.

For soot formation, the study of reactive crosslinking between aromatic soot precursors has been extended with colleague **Angiras MENON** to include kinetic rates and equilibria. This allows the various rates to be compared between small

*Fig. 3.5: Low energy clusters of flat and curved aromatic molecules. .*

Dr Jacob Martin
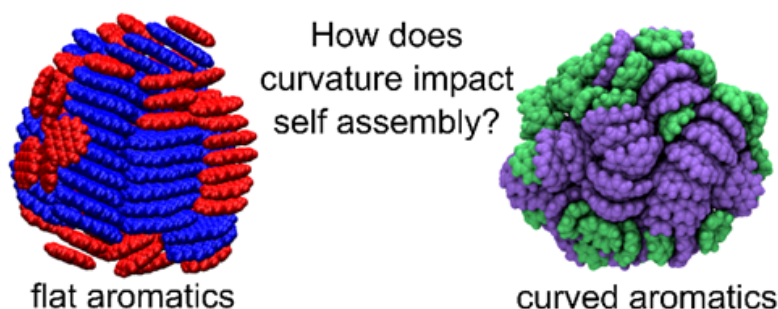
reactive aromatic soot precursors. None of the rates were found to be rapid enough to explain the formation of soot, however, localised π-radicals were found to be significantly enhanced due to physical interactions. We are currently exploring the significance of such an enhancement and what impact it could have on soot formation.

Recent experimental work was also published with Dr Maurin SALAMANCA showing the role of pentagonal fuels on increasing the curvature of soot's nanostructure and increasing the production of soot that is supported by the recent exploration of reactive edges and flexoelectricity (see Figure 3.6).

A review of soot formation is still undergoing integrating new mechanisms for soot formation with the studies of crosslinking reactive aromatics as mentioned (see the focus on fundamental science article earlier in this document). Dr Jacob Martin has since graduated from his PhD and has accepted a fellowship in Perth, Australia to explore carbon materials for energy storage.

Angiras MENON's (PhD student, CAM) work

focuses on using *ab initio* quantum chemical
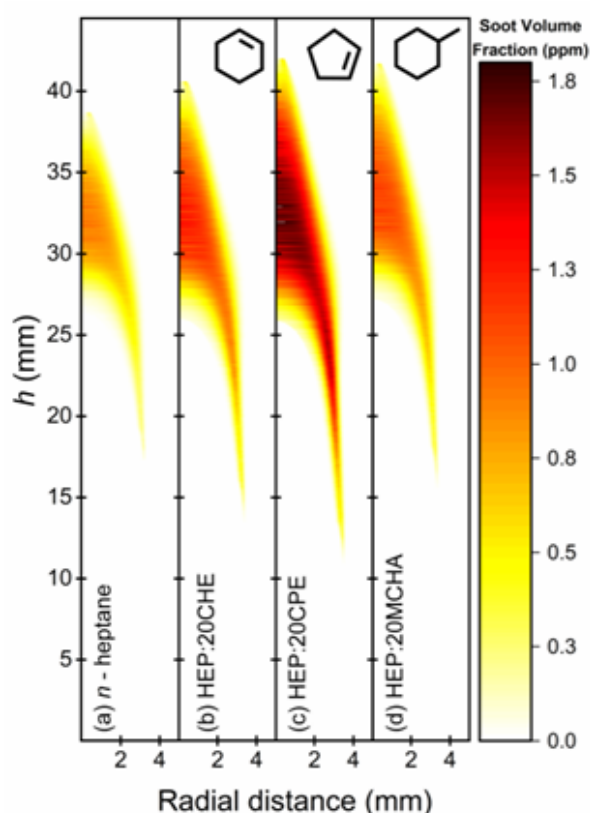
methods to understand the optical, kinetic and thermodynamic properties of polycyclic aromatic hydrocarbons (PAHs). The key aim is to understand the role of PAHs in forming carbonaceous nanoparticles in flames.

A project with Dr Jacob Martin has been completed that analyses the reactivity, electronic structure and concentration of localisedπ-radical PAHs. It has been shown that localised π-radicals are present in significant concentrations at soot nucleation temperature and that multiple localised π-radical sites could exist on a single larger PAH, which could allow for chemical chain reactions to occur.

In a recent project, also with Dr Jacob Martin, the rates of bridge-forming (cross-linking) reactions between PAHs containing different edge types have been computed (see Figure 3.7). This work has suggested that the reactions between aryl-type σ-radical PAHs and localised πradical PAHs are potentially faster than bridge-forming reactions between other edge types. Such reactions also have substantial equilibrium constants, meaning they are expected to be highly favourable at flame temperatures.

Additionally, analysis of bridge-forming reactions for larger PAHs that can bond and stack showed that larger localised π-radical PAHs have a substantial enhancement in equilibrium constants due to the rim bonding (see Figure 3.8). This highlights the potential importance of combined chemical bonding and physical interactions between PAHs. This work has suggested that rim bonding between localised πradical PAHs could be an important mechanism to consider for soot formation and has been submitted for publication.

Fig. 3.6: Doped heptane flame soot volume fractions determined from two colour pyrometry. The impact of cyclic fuels on the formation and structure of soot. Maurin Salamanca, Maria Botero, Jacob Martin, Jochen Dreyer, Jethro Akroyd and Markus Kraft, Combustion and Flame 219, 1-12, (2020).
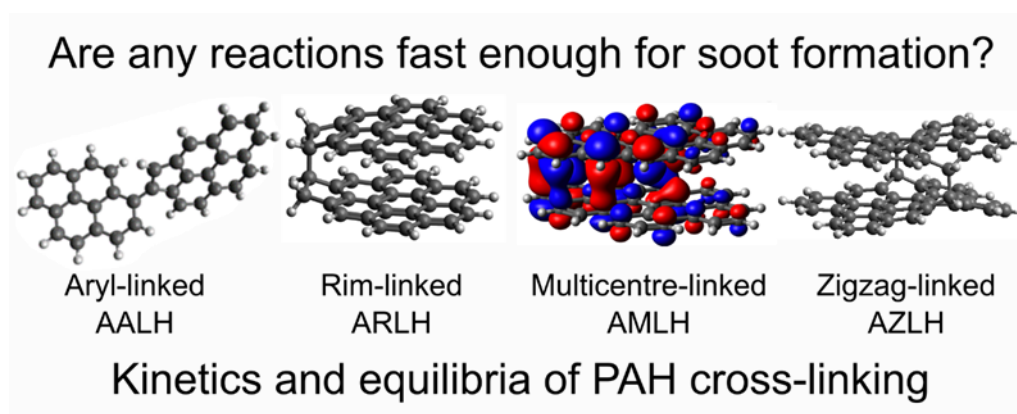
Fig. 3.7: Spin density isosurface (blue) and value of atom with highest Milliken spin density .

Angiras MENON
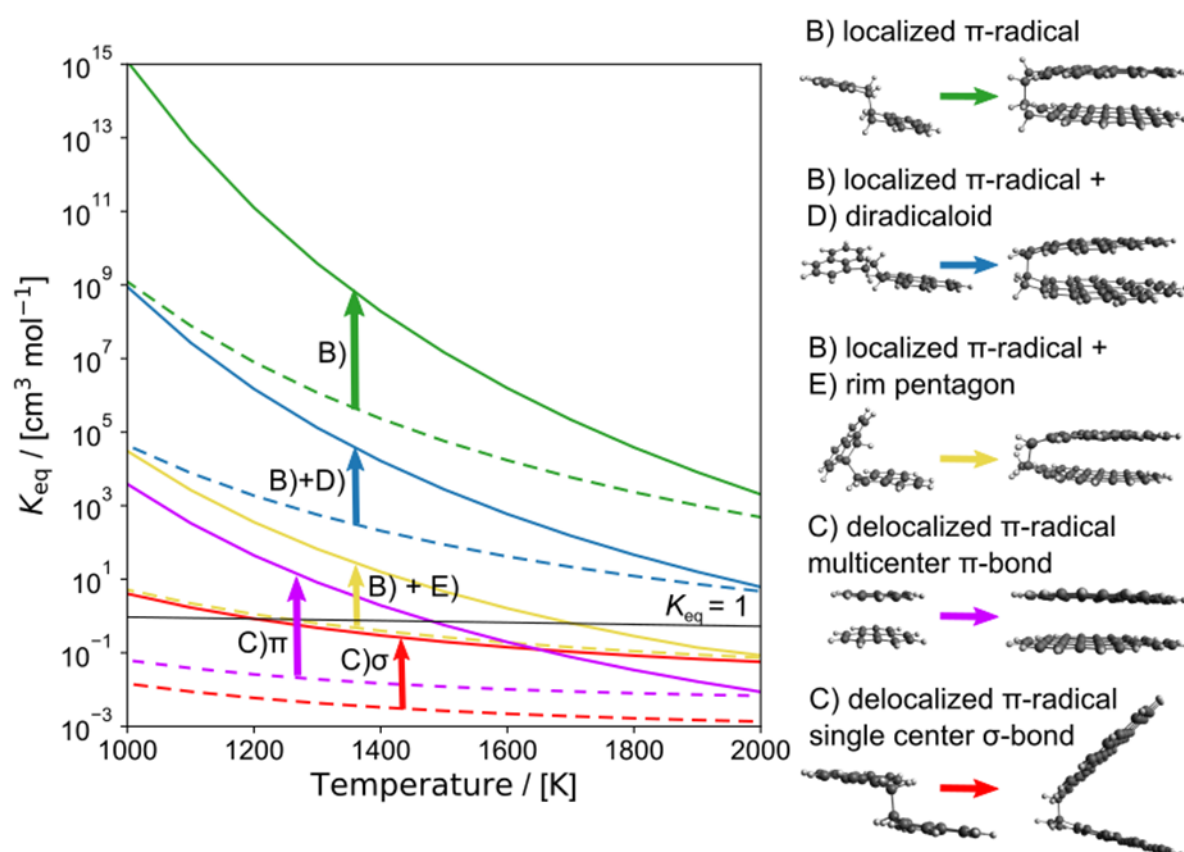
Fig. 3.8 Equilibrium constants for cross-linking reactions between larger PAHs that can result in bonded and stacked structures. The dashed lines represent the equilibrium constant for smaller PAHs with the same reactive edge types, and the arrows represent the enhancement effect. The results suggest that localised pi-radical PAHs have the most substantial enhancement effect due to bonding and stacking.

Angiras MENON

Update on work package 3.3

Better, cheaper, cleaner nanostructures — experimental
Flame synthesis of thin films of mixed metal oxide nanoparticles

During the current reporting period **Dr SHENG Yuan (Research Fellow, NTU)** focused on improving the oxygen evolution stability of flame-synthesised Ni-Fe phosphides. The leaching of Fe from the catalyst was identified as a major factor in performance degradation. To mitigate this issue the chemical composition of both the electrode substrate (Fe versus Ni) and the catalyst (Ni/Fe/Cu content) was carefully tuned. Thus the degradation rate, in terms of increase in overpotential at a current density of 500 mA/cm² in 1 M KOH, was reduced by half to 0.25 mV/h. In order to enhance the efficiency of the flame synthesis experiments and their potential for scale-up, Dr Sheng Yuan developed liquid precursor formulations to replace the solid precursors used previously. It allows fast switching of the type of precursors and eliminates the need to clean/refill the precursor delivery system in every experiment. Moreover, he designed and constructed an in-house plug flow reactor system for the performance evaluation of flame-synthesised catalysts in petrochemical processes.
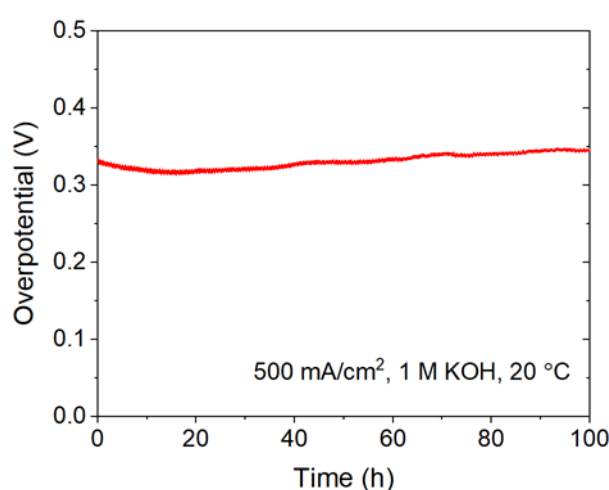

Fig. 3.9: Oxygen evolution stability of a flame-synthesised Ni-Fe-Cu phosphide catalyst

Dr SHENG Yuan (unpublished data)

WU Shuyang's (PhD student, NTU) main research interest lies in the area of flame synthesised defective TiO_2 for CO_2 photoreduction and gaseous isopropyl alcohol (IPA) photo-oxidation. Over the past few months, his research has mainly focused on the study of *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) which investigates the reaction mechanisms of CO_2 photoreduction and IPA photo-oxidation on flame-made TiO_{2-x} samples. In this work, the *in situ* DRIFTS analysis results indicate that the presence of surface defects could efficiently promote CO_2 adsorption and conversion, leading to enhanced CO generation rate. The detection of CO_2^- intermediate species suggests that single electron transfer to CO_2 molecules occurs on defective TiO_2, making the activation of stable CO_2 molecules much easier. In contrast, less spectral change and no CO_2^- signal are observed on defect-free P25 TiO_2 which suggests the CO_2 activation is difficult to take place on perfect TiO_2 surface. The IR spectral change indicates the three carbon containing species (CO_2^-, b-CO_3^{2-} and HCO_3^-) may act as primary intermediates in the photoreduction of CO_2 to CO and H_2O may contribute to the reaction by donating electrons or holes. In the IPA photo-oxidation study, the *in situ* DRIFTS results demonstrate that the presence of OVs in TiO_{2-x} could notably facilitate the degradation of IPA to acetone and subsequent conversion to formate and acetate intermediates. The mineralisation of such intermediates to the final product CO_2 is the rate-limiting step for the reaction on TiO_{2-x}-20 min. This work demonstrates the flame-made TiO_{2-x} is an efficient photocatalyst for IPA oxidation under visible light. This flame synthesis technique could be further extended to other non-stoichiometric semiconductors, intended for photo-degradation of various VOC pollutants for air purification.

Since the bands at 1550 and 1535 cm⁻¹ overlapped with each other, the band at 1443 cm⁻¹ was used to identify the presence of acetates and the band at 1360 cm⁻¹ was used to prove the existence of formate. However, the band for acetone at 1699 cm⁻¹ only has a slight increase probably due to the subsequent rapid conversion to the intermediate species. The acetone molecule could be attacked by the charges and break into a two-carbon species and a single carbon species, which are identified as the acetate and formate in the spectra. The rapid increment of formate bands at 1550, 1360 cm⁻¹ and the acetate bands at 1535, 1443 cm⁻¹ demonstrates the formation of formate and acetate species from acetone is very fast on TiO_{2-x}-20 min. However, it has been reported that

only formate species can be converted to CO_2 instead of acetate. Acetate would be first decomposed to formate and then form CO_2. It was found that formate and acetate species are accumulated on TiO_2 surface until they reach steady-state concentration at the 4th hour. This result indicates the rate-limiting step of IPA photooxidation on TiO_{2-x}-20 min is the mineralisation of formate and acetate to CO_2. The CO_2 band at 2345 cm⁻¹ can be observed from the second hour and accumulate to a constant value due to the subsequent desorption. No obvious reduction of formate and acetate bands and low intensity of CO_2 band prove that the conversion of such compounds to CO_2 is a sluggish process.
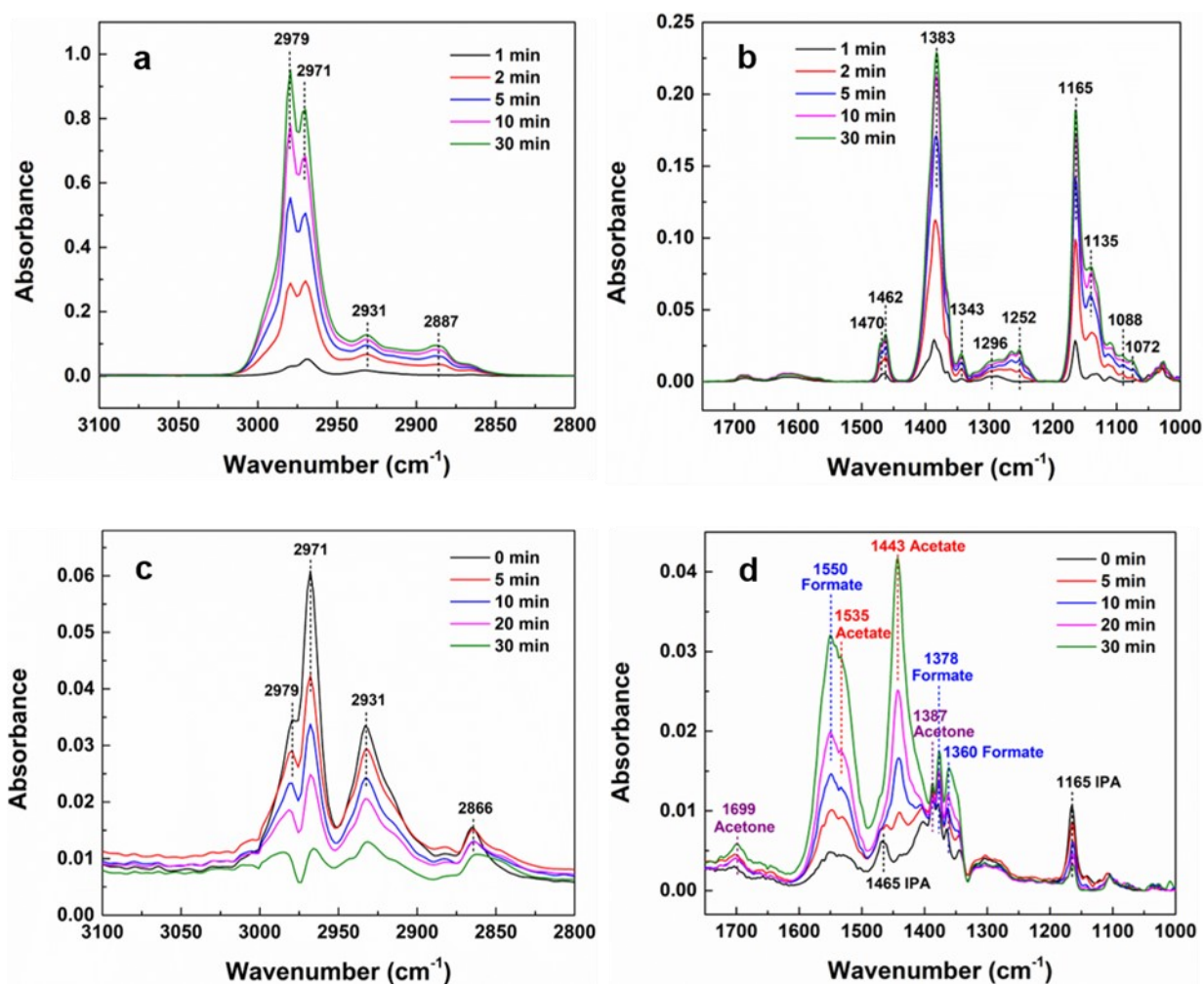

Fig. 3.10: (In situ DRIFTS spectra for TiO_{2-x}-20 min in the dark (a) and (b); under light irradiation (> 400 nm) (c) and (d).

WU Shuyang

Update on work package 3.4

Better, cheaper, cleaner nanostructures — modelling

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

Dr Manoel MANUPUTTY (Research Fellow, NTU) started as a Research Fellow in Prof. XU Rong's group in August. Building on his PhD work, he is working on using flame synthesis methods to prepare novel metal oxide nanoparticles/films for applications such as photocatalysis or catalyst support. Recently, he is focusing on the characterisation of TiO_2 and Nb-doped TiO_2 film morphologies using scanning electron microscopy. In addition, he is exploring a multinozzle flame deposition approach to perform a soot-templated synthesis of mesoporous TiO_2 films. One of the possible applications of such material is for superamphiphobic coating. Separately, Dr Manoel Manuputty is also working on

flame and nanoparticle characterisations using chemiluminescence and differential mobility spectrometry to investigate particle growth and coagulation. This is in collaboration with Eric BRINGLEY, a PhD student from Cambridge who is working on developing the computational fluid dynamics model of the stagnation flames.

Figure 3.11: The chemiluminescence setup to image thermally excited species such as CH* and OH* in a premixed stagnation flame.

Dr Manoel MANUPUTTY
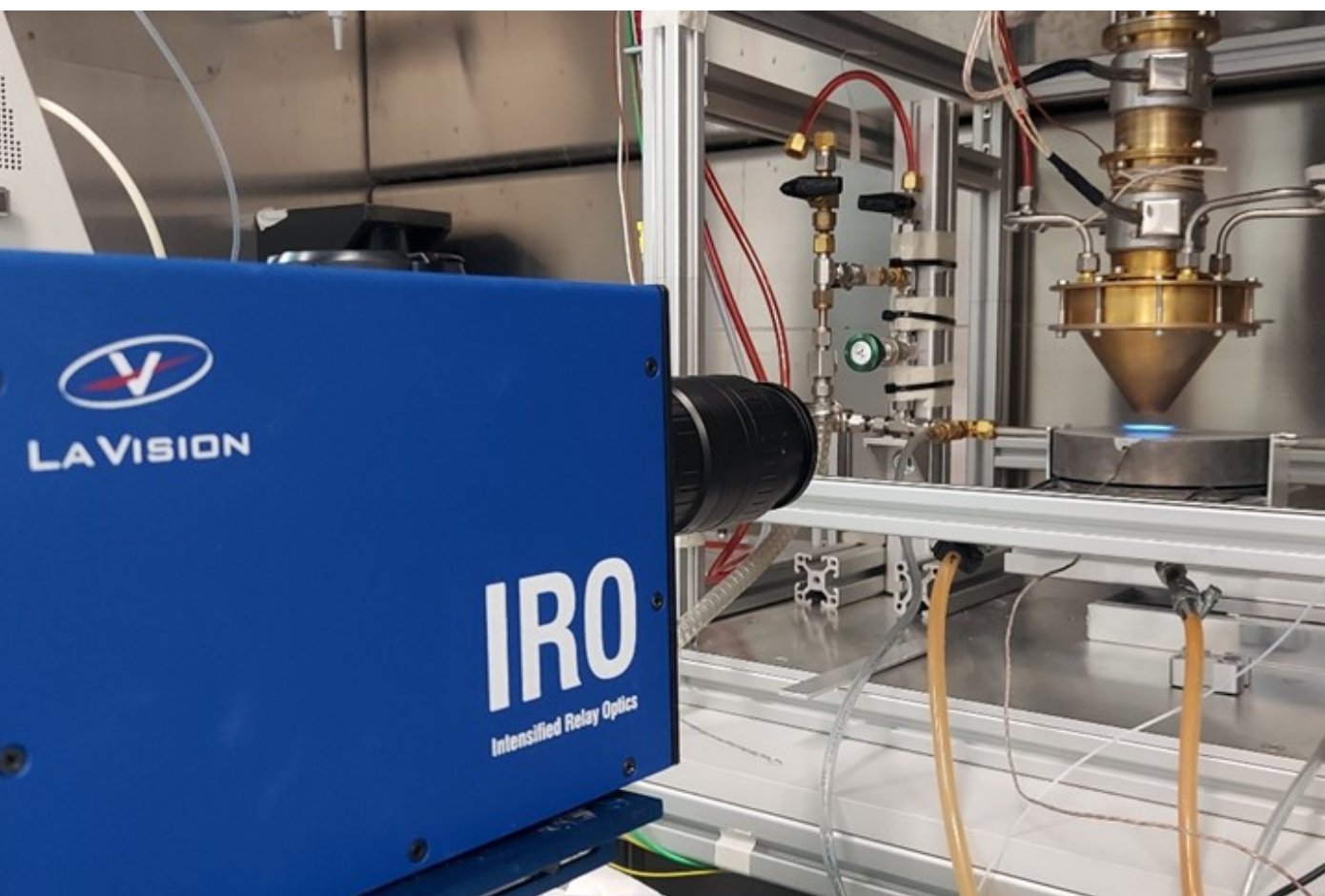
Scientific output

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 17.

An assessment of the viability of alternatives to biodiesel transport fuels

Rebecca Kächele, Daniel Nurkowski, Jacob W. Martin, Jethro Akroyd and Markus Kraft , *Applied Energy*

DOI: 10.1016/j.apenergy.2019.113363

Abstract: his work presents an economic feasibility study of using algae and biochar burial strategies to offset carbon emission from the use of conventional fossil-derived transport fuels. The economic feasibility is quantified on the basis that the final price of the decarbonised fossil-derived diesel should be lower or equal to the price of biodiesel which is deemed to be the next best alternative. The extra costs associated with the carbon capture/offset via algae and biochar burial are estimated for the most typical scenarios using the economic models developed as part of this work. In addition, High Dimensional Model Representation based global sensitivity analyses are performed in order to quantify the influence of key model parameters on the overall costs. It was found that using algae burial to offset carbon emissions is not viable for principle reasons such as the amount of water required and the burial of phosphate as well as more than doubling the current diesel price. This price is mainly due to the high costs of pumping dilute algae slurry underground. The biochar burial approach, on the other hand, was found to be much more economically viable as it only increases the conventional diesel price by a small amount. This comparably low price is due to the revenue generated from selling the electricity produced from the pyrolysis by-products. In addition, the global sensitivity analysis revealed that the overall costs were the most sensitive to the wood price, as the wood feedstock may either be an income or an expenditure.
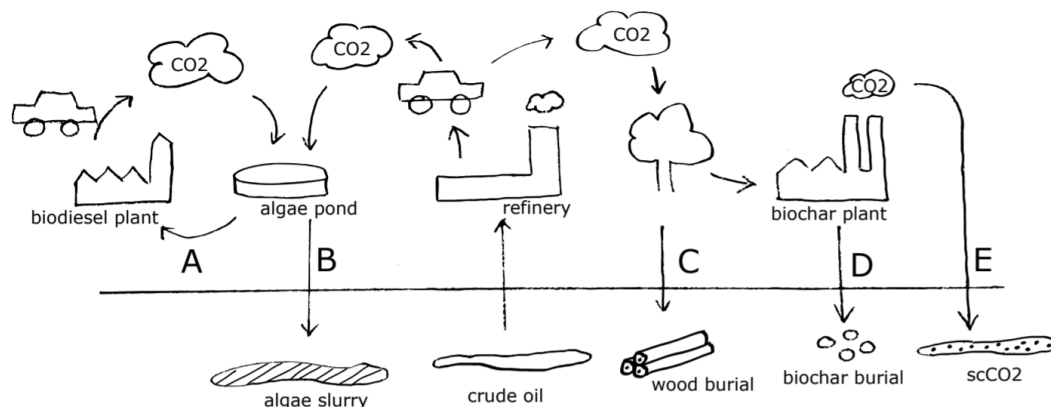
Investigation of the Impact of the Configuration of Exhaust After-Treatment System for Diesel Engines

Chung Ting Lao, Jethro Akroyd, Nickolas Eaves, Alastair Smith, Neal Morgan, Daniel Nurkowski, Amit Bhave and Markus Kraft, *Applied Energy*

DOI: 10.1016/j.apenergy.2020.114844

Abstract: Exhaust After-Treatment (EAT) systems are necessary for automotive powertrains to meet stringent emission standards. Computational modelling has been applied to aid designing EAT systems. Models with global kinetic mechanisms are often used in practice, but they cannot accurately predict the behaviour of after-treatment devices under a wide range of conditions. In this study, a numerical EAT model with rigorous

treatment of the catalytic chemistry is proposed to investigate the impact of the configuration of individual devices in the EAT system; one of the key design decisions. The performance of the proposed model is first critically assessed against experimental and simulation data from the literature before being applied to design a multi-device EAT system for a diesel engine. The target EAT system is composed of a diesel oxidation catalyst (DOC), an ammonia-based selective catalytic reduction (NH3-SCR) device and a diesel particulate filter (DPF). The steady state behaviour of various EAT designs under operating conditions across the engine map are examined. The DOC-DPF-SCR layout is found to be more beneficial than the alternative DOC-SCR-DPF for the specific engine studied. Furthermore, the DPF-front system is more robust with respect to

changes in emission regulations. Flux analysis is applied to study the chemical interaction in the SCR and explain the disadvantage of the SCR-front system. In addition, it is demonstrated in the study that future catalyst investigations should consider more realistic feed compositions.
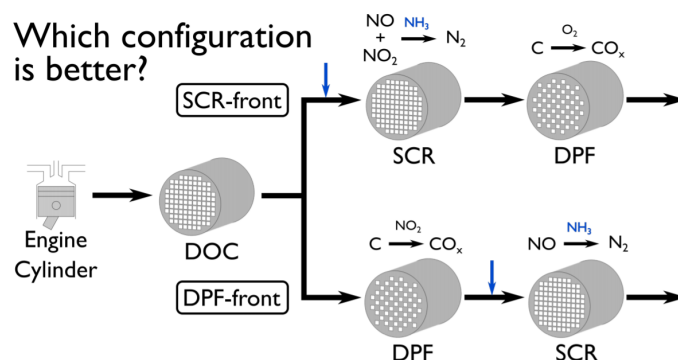

Detailed characterisation of TiO₂ nano-aggregate morphology using TEM image analysis

Manuputty, Manoel Y., Casper S. Lindberg, Maria L. Botero, Jethro Akroyd and Markus Kraft
Journal of Aerosol Science

Abstract: A detailed morphological characterisation is performed on TiO2 nano-aggregates synthesised in a premixed stagnation flame using transmission electron microscopy (TEM) image analysis. The size-dependent collection efficiency of the TEM sampling method is accounted for with a simple correction for particle deposition through impaction and diffusion. The TEM-derived sizes show excellent agreement with electrical mobility measurements. Primary particle size, aggregate size, and degree of aggregation distributions were obtained for two different flames and varying precursor loading. The degree of aggregation is defined as the ratio of gyration to spherical equivalent sizes from the projected area analysis, allowing identification of particles with spherical and non-spherical morphologies. The size distributions are found to be strongly affected by precursor loading but not by flame mixture or maximum temperature. In all cases, approximately 60-70% particles have spherical morphology while the rest form small aggregates. Aggregation is likely to occur only very late in the growth stage, leading to the similarity between the primary particle and spherical particle size distributions. The detailed morphological information reported provides the much-needed experimental data for studying the early stage particle formation of TiO2 from titanium tetraisopropoxide (TTIP) in a well-defined burner configuration.
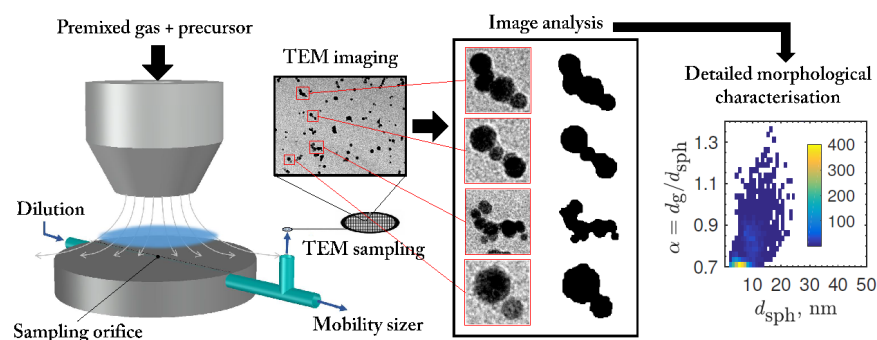
## Dynamic polarity of curved aromatic soot precursors

Jacob W. Martin, Angiras Menon, Chung Ting Lao, Jethro Akroyd and Markus Kraft, *Combustion and Flame*

Abstract: In this paper, we answer the question of whether polar curved aromatics are persistently polar at flame temperatures. We find, using electronic structure calculations and transition state theory, that the inversion barriers of curved aromatics (cPAH) of 0.9-1.2 nm in diameter are high and that they are not able to invert over the timescales and at the high temperatures found in sooting flames. We find a transition for smaller curved aromatics between 11-15 (≈0.8 nm) rings where the increasing strain introduced from the pentagonal ring increases the inversion barrier leading to rigidity. We then performed ab initio quantum molecular dynamics to find the molecular dipole fluctuations of a nanometre-sized cPAH at 1500 K. We found the bending mode of the bowl-shaped molecule gave rise to the largest fluctuations on the dipole moment by ±0.5-1 debye about the equilibrium value of 5.00 debye, indicating persistent polarity. We also observed binding of a chemi-ion at 1500 K over 2 ps, suggesting the molecular dipole of cPAH will be an important consideration in soot formation mechanisms.

Are curved PAH persistently polar in a flame?
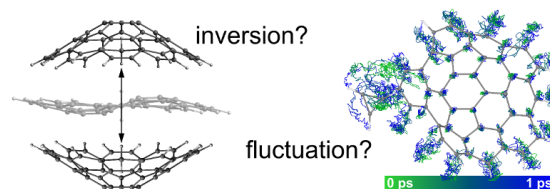
## A density functional theory study on the kinetics of seven-member ring formation in polyaromatic hydrocarbons

Menon, Angiras, Gustavo Leon, Jethro Akroyd, and Markus Kraft, *Combustion and Flame*

Abstract: In this work, the kinetics of seven-member ring formation in PAHs containing a five-member ring is studied by density functional theory. The pathways studied include integration of a seven member ring by the hydrogen-abstractionacetylene-addition (HACA) mechanism for two different PAHs, one closed shell and one resonance-stabilised-radical (RSR) PAH. The pathways were similar in both cases, but the rate of seven-member ring formation by HACA was seen to be faster for the resonance-stabilised-radical PAH. Formation of a seven member ring by bay closure processes facilitated through hydrogen abstraction, hydrogen addition, carbene formation, and direct cyclisation were also studied for two PAHs. In general, the pathways were rather similar for both PAHs, aside from the direct cyclisation route. The rate constants determined for the pathways were then used in kinetic simulations in 0D homogeneous reactors. The results showed that for the RSR PAH, the initial abstraction site is important, with the seven-member ring mainly being formed when abstraction occurs near the five member ring. This was not the case for the closed shell PAH. For the bay closures, it was seen for both PAHs that the hydrogen abstraction facilitated bay closures contributes the most to seven-member ring formation at temperatures up to 2000 K, but for very high temperatures of 2500 K, the carbene route becomes the most important contributor. The formation of seven-member rings occurred within 1 ms for all cases studied in the 0D reactors, suggesting that seven-member ring formation in PAHs containing a five-member ring is possible at flame temperatures.

Rates of 7-member ring formation in PAHs

Bay Closures

HACA
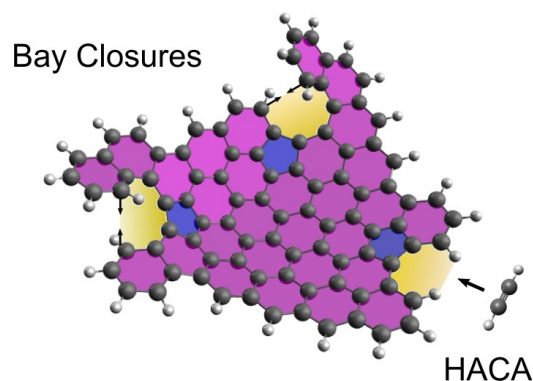
The impact of cyclic fuels on the formation and structure of soot

Maurin Salamanca, Maria L. Botero, Jacob W. Martin, Jochen A.H. Dreyer, Jethro Akroyd and Markus Kraft, *Combustion and Flame*

Abstract: This paper investigates the impact of cyclic fuels on the nanostructure, nucleation and overall production of soot in an n-heptane (C_7H_{16}) laminar coflow diffusion flame. The fuels selected to dope the n-heptane flames are cyclopentene (C_5H_8), cyclohexene (C_6H_{10}) and methylcyclohexane (C_7H_{14}). These fuels were chosen for their differences in their structure and sooting tendency. The flame structure was studied with Differential Mobility Spectrometry (DMS) for particle size distribution determination, two-colour ratio pyrometry to calculate the soot volume fraction and soot temperature. The soot nanostructure was investigated using Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM). The addition of cyclic fuels was found to promote the formation of soot nanoparticles earlier in flames. In addition, the soot volume fraction was increased significantly by the addition of the cyclic fuels, especially by the addition of cyclopentene. The addition of 20% of cyclopentene increased the soot volume fraction by a factor of 2. HRTEM results suggest a significant influence of cyclopentene on the soot nanostructure; cyclopentene addition promotes the incorporation of five-membered rings (pentagonal rings) leading to highly curved fringes. This suggests cyclopentene could be used as a fuel to promote curvature in different carbonaceous structures to modify their properties.
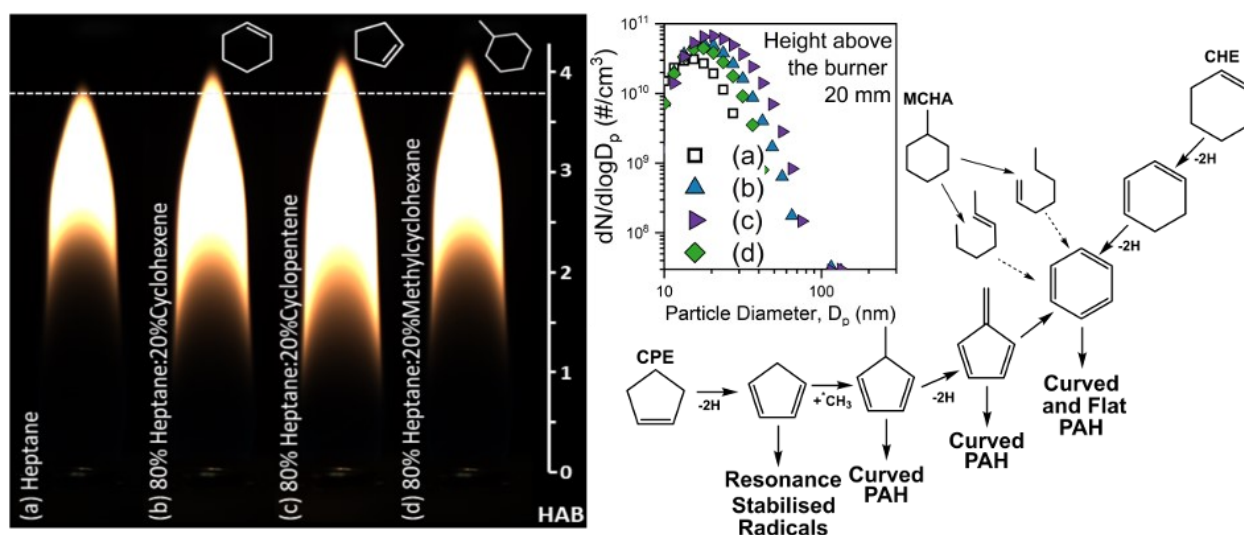
Other activities and achievements

Research Fellow Dr Jacob MARTIN gave a presentation to the Churchill College MCR called 'The Chemical History of a Candle and Structure of an Ember'.

He also gave a talk (with experiments included) to several classrooms of Year 6 students on 'Understanding Candles for Cleaner Air', based on Faraday's lectures on the chemical history of a candle.

PhD student Angiras MENON gave an online presentation for the Johnson Matthey Academic Conference on 18th June 2020. The talk was titled 'Multiscale Modelling of Soot Formation' and was presented to members of Johnson Matthey's research and development division as well as other PhD students sponsored by Johnson Matthey.

Research Fellow Dr SHENG Yuan gave a virtual poster presentation titled 'Rapid flame aerosol synthesis of Ni-Fe phosphide anode for alkaline water electrolysis' at the *Materials for Space Exploration MAPEX Symposium 2020* (31 August – 2 September. (Other authors: Markus KRAFT and XU Rong.)

PhD student WU Shuyang gave a virtual poster presentation titled 'Premixed Stagnation Flame Synthesized TiO_2 Nanoparticles with Mixed Phases for Efficient Photocatalytic Hydrogen Generation' at *The 8th Asia Pacific Congress on Catalysis (APCAT-8)*, 4-7 August. (Other authors: TU Wenguang, YIN Shengming and XU Rong.)

PhD student Kimberly BOWAL gave a virtual presentation titled 'Surface properties of heterogeneous polycyclic aromatic hydrocarbon clusters' at the *Cambridge Particle Meeting*, 19th June. (Other authors: Laura PASCAZIO, WANG Hongyu, CHEN Dongping and Markus KRAFT.)

PI Prof. Markus KRAFT gave an online webinar titled 'Carbonaceous nanoparticle formation in flames' which highlighted the group's recent research on soot formation. The Combustion Webinar series was organised by the combustion science community to enable the opportunity to interact technically while in-person conferences are on hold. Talks so far have covered fundamental combustion science and diagnostics, as well as the future of the internal combustion engine.
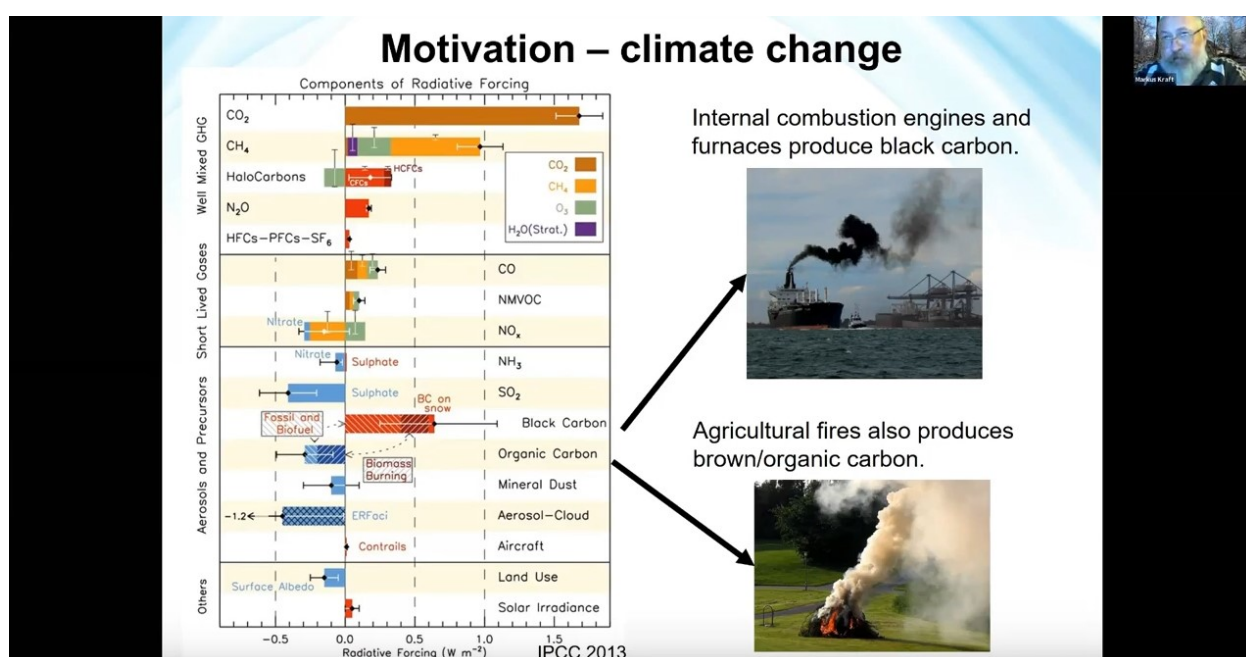
Prof. Markus KRAFT giving his Combustion Webinar presentation.

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 push for better energy efficiency, lower pollution, and decarbonisation in the marine sector is increasing in pace and importance worldwide. This IRP addresses these significant problems by a series of connected work packages, including fundamental studies on particulate emissions from marine engines burning fossil or alternative fuels, waste heat utilisation methods such as the use or Organic Rankine Cycles and the associated turbomachinery, high-efficiency heat exchangers, and estimates and measurements of pollutant dispersion from ships and its reception in port and urban areas.

In WP1, significant progress has been made in analysing computationally the combustion process in a model marine engine. Multi-dimensional Computational Fluid Dynamics (CFD) simulations have been performed and the soot production and oxidation processes have been analysed. A detailed comparison with experimentally-observed trends shows good agreement. In WP2, a novel closed power cycle for harnessing waste heat has been studied thermodynamically and the associated turbomachinery developed; such power cycles are currently of interest for data centres and efforts are being made to adapt them for marine engine waste heat. In WP3, new heat exchanger geometries have been developed. In WP4, an integrated approach for dispersion of ship emissions is taken, where the near-field and the far-field are separately studied, and the methodologies to include moving sources (as from a moving ship) in regional-scale atmospheric dispersion models are developed. Full integration in JPS and validation with experimental data is progressing.

The work is proceeding to plan and research results are already being produced for publications and disseminated in good international conferences.

Professor Epaminondas Mastorakos, PI
University of Cambridge

Update on work package 4.1
Engine combustion — best fuel, best operating condition

Shrey TRIVEDI (Research Assistant, CAM) performed simulations of a heavy-duty research engine MTU396 using CFD code STAR-CD coupled with an in-house 3D Condition Moment Closure (CMC) code. This engine contains seven identical injector holes and only the section of engine containing a single injector hole was simulated. This setup is shown in Figure 4.1 (left) with the help of the snapshot of the temperature field in the engine at the top dead centre (TDC). Dodecane was used as a surrogate for Diesel spray and n-heptane chemistry was used for combustion. URANS was employed for turbulence modelling. For the reference case, the Start of Injection (SOI) was at -10 degrees Crank Angle (CA) and Duration Of Injection (DOI) was 2ms. Several variations were considered from the simulations,

namely: 1) SOI variation: -6 degrees CA, -10 deg. CA (reference case) and -14 deg. CA, 2) DOI variation: 1ms, 2ms (reference case) and 3ms and 3) Oxidiser variation: 21% O_2 (reference case), 18% O_2 and 15% O_2. Soot and NOx for these variations was found to follow the trends consistent with the previous literature. Two-dimensional slices of mixture fraction, soot mass fraction and soot precursor C_2H_2 at 10 degrees CA after SOI are shown in Figure 4.1 (right).

These results are currently being prepared for publication. In addition, development of integrating CMC with CFD code CONVERGE is also underway. The automatic mesh generation and refinement in CONVERGE will be very useful for efficient simulations of engines in future.
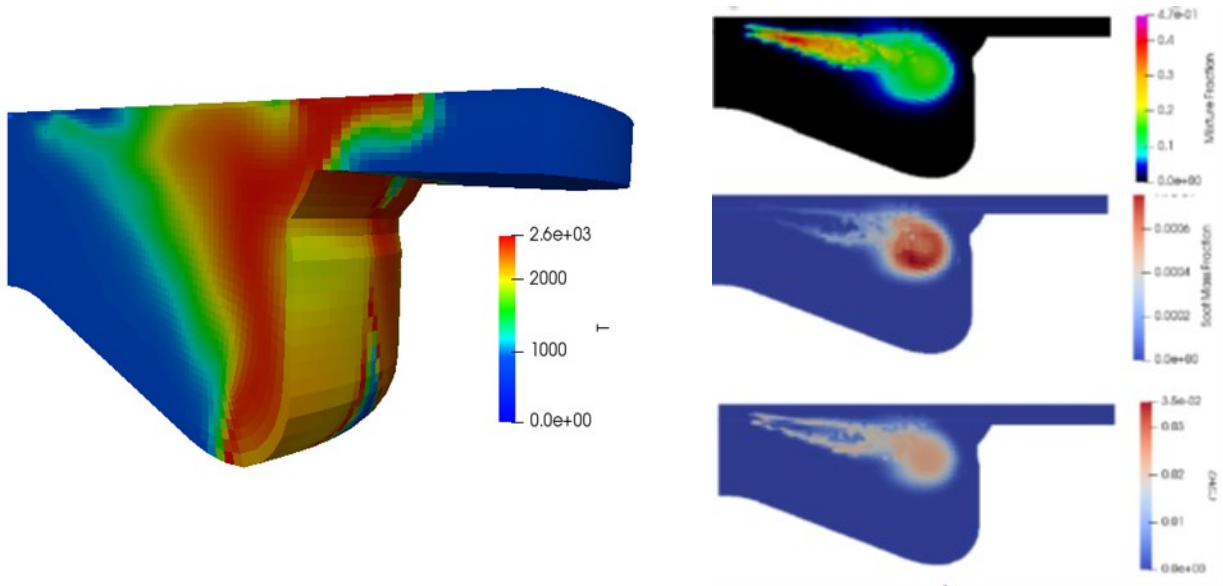

Fig. 4.1: (left) Section of engine cylinder simulated using STAR-CD. Colourmap shows temperature. (right) 2D slices of mixture fraction, soot mass fraction and soot precursor C_2H_2 at 10 deg. CA after SOI.

Shrey TRIVEDI

Update on work package 4.2
Closed power cycles — selection and analysis

Dr Zheng LIU's (Research Fellow, NTU) main research interest lies in the design and modelling of radial flow gas turbines. Over the past six months, he has been working on the development of high efficiency two-stage cryogenic turbine expanders. As shown in Figure 4.2, the turbine expander consists of three main parts – the volute, nozzle and rotor. Each part has a unique function and a crucial impact on the efficiency and flow performance of the device. The cryogenic turbine expanders utilise high-pressure nitrogen as the working fluid, and are designed to produce the total rated electric power of 1.56 megawatt at an overall expansion ratio over 100. To achieved this design requirement, Dr Zheng Liu has developed a turbine design-analysis framework, which automates the process from the generation three-dimensional geometries to the evaluation of aerodynamic performance. To find the suitable designs, more than 1000 turbine designs were generated, where each design has

24 design parameters considered. To reduce the development time, the framework was integrated with the high performance computing (HPC) clusters in NTU, such that the averaged development time for each design is reduced to 25 minutes approximately.

Figure 4.3 shows a typical turbine performance map based on one design produced by the design framework. It shows that the turbine can produce a high efficiency of over 80% at the expansion ratio of 10 and rotational speed of 24.45 krpm. Another advantage is that the turbine can maintain a relative stable efficiency at a higher expansion ratio, which lead to a good off-design performance. Based on the actual design, Dr Zheng Liu has conducted finite element analysis (FEA) in order to find the most suitable material that can endure the high stresses caused by the high speed rotation and the high pressure flow field.
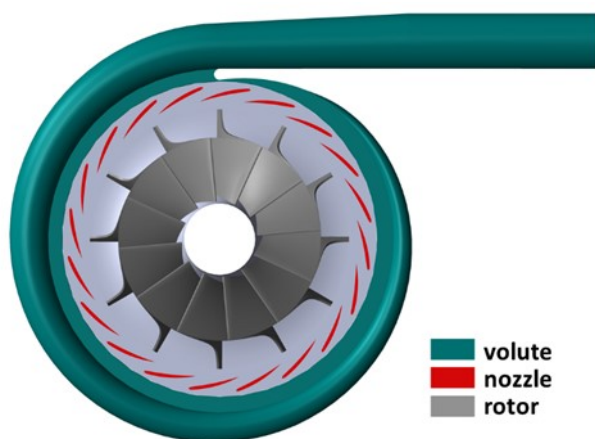

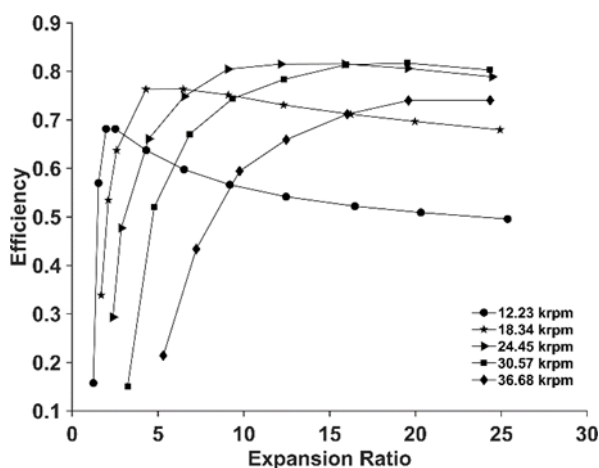*Fig. 4.2: The assembly of a radial gas turbine.*

Fig. 4.3: Typical turbine performance map.

Update on work package 4.4
Process system model for the J-Park Simulator

Dr Kang PAN (Research Fellow, CARES) has recently conducted a case study to compare the use of the new developed emission source model, namely a moving point source (MPS) model, with the commonly used emission source models (fixed point source and line source models) in shipping emission dispersion modelling. The simulation was conducted in Singapore area with simplified computational setups (such as constant weather condition), and all the ships are assumed moving at a constant speed and direction in the simulation, as shown in Figure 4.4.

Based on the instantaneous NO_2 concentration predicted by using the different emission source models as shown in Figure 4.5, it is evident that the moving point source model predicts a different distribution compared to the other two mod-

els. Since the ships are always moving and generate the emission plumes at different locations, the moving point source model has the ability to update the ships' positions and hence predict a more realistic emission profile. In comparison, a line source model assumes a continuous emission release along the entire moving route for each ship, while a fixed point source model assumes the ship position is unchanged. As a result, both the fixed point source and line source models are not suitable for predicting the instantaneous distribution of emissions released from the moving ships. The newly developed moving point source model has been integrated to the J-Park Simulator to evaluate the shipping emission effects on the coastal cities, such as Singapore and Hong Kong.

(a) *The initial ship position at t=0 min*   (b) *Ship movements during t = 0-60 min*
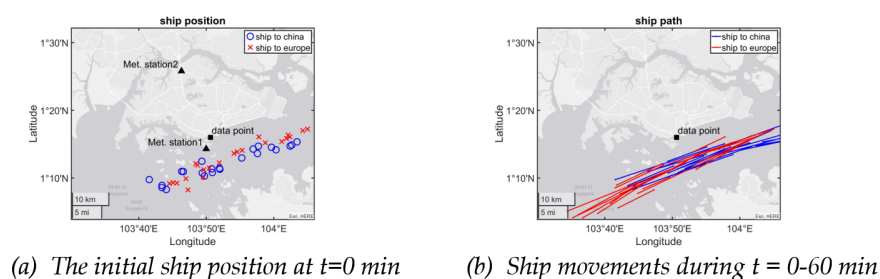
Fig. 4.4: Configuration of the simulation domain in Singapore.

Symbols: ships to China (blue circles) and ships to Europe (red crosses); Lines: ship routes

(a) *Moving point source*   (b) *Line source*   (c) *Fixed point source*
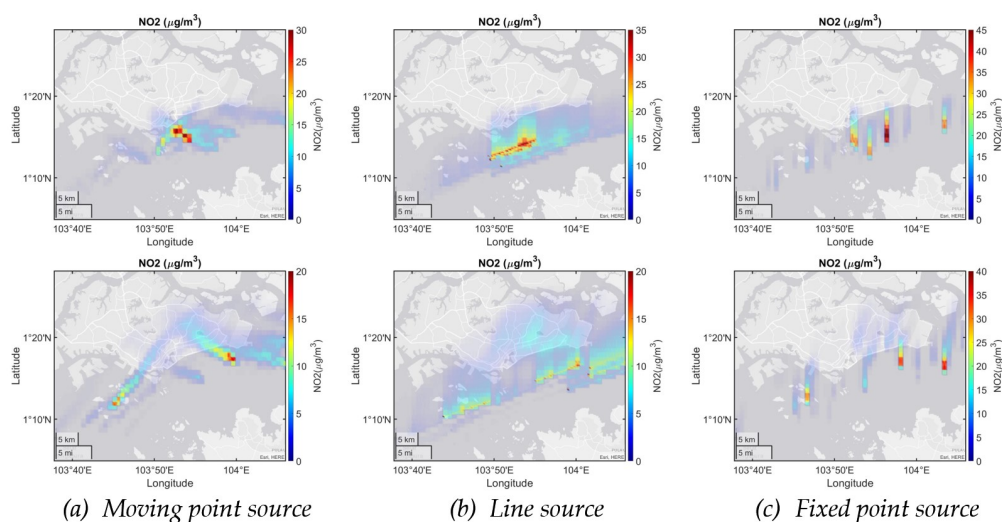
Fig. 4.5: Comparison of instantaneous NO_2 profiles for moving ships by using different source types. Top: t=0-60 mins; Bottom: t=60-120 mins.

In the next stage of Dr Kang Pan's work, a CFD simulation of a diesel engine (located in the NUS engine lab) by using different types of fuels will be conducted. In the first step, the 3D engine computational model will be built up by using STAR-CD CFD package, based on the geometry of the NUS engine (especially the engine piston) captured by the 3D scanning, as shown in Figure 4.6.
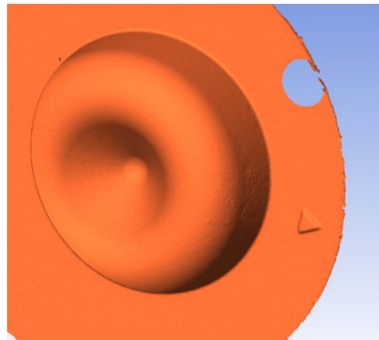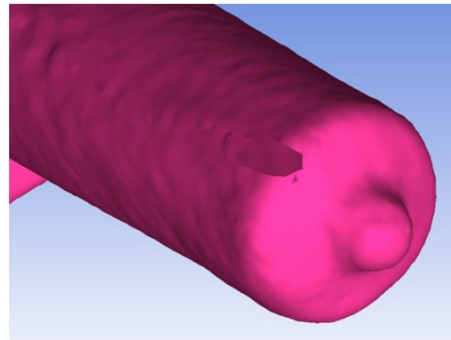
(a) piston   *(b) injector*

Fig. 4.6: **3D drawings of piston and injector used in NUS diesel engine** .

Dr Kang PAN

Other activities and achievements

Research Fellow Dr ZHENG Liu presented his research work titled 'Optimization of Vaneless Volute and Mixed Flow Impeller for Pulsating Flow' at the virtual conference ASME *Turbo Expo Turbomachinery Technical Conference & Exposition* (21-25 September).

Dr ZHENG Liu has also been awarded the PhD degree and promoted to Research Fellow.

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

Over the past six months, the IRP BB team has made further progress on identifying the factors that can encourage businesses to adopt sustainable innovations and technologies. BB and IRP2 are also working together to investigate how to optimise the use of renewable energy that could be generated on-site by local electrochemical manufacturers.

A survey that will measure attitudes towards clean technology adoption has been refined and is ready for release to organisations. As well as yielding publishable data, the survey will provide a foundation from which BB can conduct further interviews on the topic of clean technology and better understand some of the barriers of its implementation. The team is also investigating this question on a global level, looking into how major international policies affect adoption of low-carbon technologies in particular countries (in this case, Singapore and China).

BB is also continuing its close collaboration with the other IRPs to identify the most promising technologies for adoption by industry.

Professor Steve Evans, PI
University of Cambridge

Update on work package BB.1
Business model innovation potentials

Research continues on evaluating alternative business models for adopting sustainable innovations and technologies. A new mathematical model was developed to extend the results on the representative consumer to the heterogeneous consumer case. In-depth theoretical and numerical investigation was conducted on the attractiveness of different business models under various scenarios. Moreover, the conditions where the heterogeneous consumers can prioritise between lease and PPA (Power Purchase Agreement) were identified.

In collaboration with IRP2, investigation has commenced of production scheduling problems that can take advantage of on-site generation of renewable energy (when available) to support local electro-chemical manufacturing. One of the underlying issues is the uncertainty and intermittency regarding on-site generation of renewable energy, e.g. solar energy. Thus, the challenge lies in how to design a mechanism to maximise the utilisation of renewable energy and minimise the inventory risk across multiple periods. This was formulated as a dynamic programming problem under joint centralised manufacturing and decentralised manufacturing that is supplied by on-site generation solar energy. Next, the IRP BB researchers will look into its extension to more complex scenarios such as multiple products and stochastic demand across multiple periods.
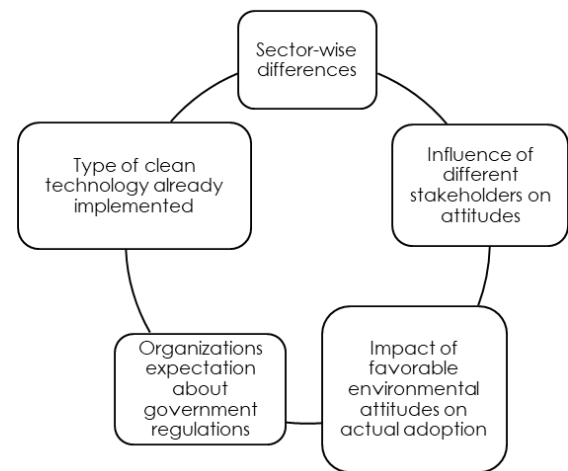

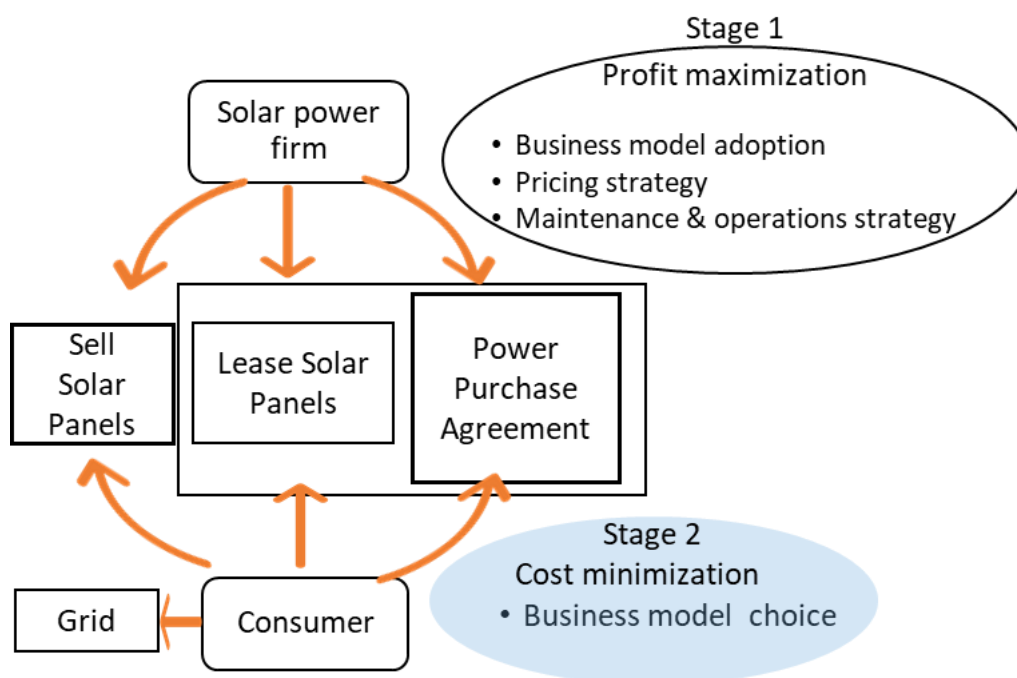*Fig. 5.1: Factors affecting adoption of clean technology.*

Fig. 5.2: Alternative business models evaluation using Stackelberg game formulation.

Update on work package BB.2
Policy formulation, customer and industry perceptions

The team is in the final stages of implementing the survey of procurement managers, technology officers and other related functional officers to gain an understanding of the willingness and attitudes of organisations towards clean technology adoption. The survey is enhanced to include the suggestions from the C4T Scientific Advisory Committee members. Currently, the team is working collaboratively with the market research agency, Blackbox, to refine the logic to implement the online survey and screening criteria to get the best quality responses. Due to COVID-19 and the associated uncertainties, C-suite candidate recruitment was put on hold to ensure minimal interference in their responses due to market uncertainties. Even though the COVID-19 situation is still pertinent, an overall better clarity on the strategic path and clean technology adoption being a long-term goal, minimal aberration is now expected. The survey will go live in the month of September and preliminary results will follow soon after. Following that, the manuscript will be written up to publish the insights gained from the survey analysis results. This survey will pave the way to two future studies: one to enhance sector-specific insights, via interviews, and second, a survey to understand the barriers towards implementation, specifically CO_2 reduction technologies (WP4).

For WP2, the team also investigated the research question: "How do international agreements and government/national policies impact the development of decarbonisation technologies and innovation capabilities of firms and industries?" We focused on two major international policies/treaties – Kyoto Protocol (1997) and Copenhagen Accord (2009) and ascertained their impacts on patented innovation in Singapore and China. Specifically, Singapore firms were compared with foreign firms based in Singapore, as well as firms listed in China and industry sectors province-level impacts in China. By comparing the innovation landscape of Singapore with that of China, a better illustration of the policy impacts in both more developed as well as emerging economies was provided.

To conduct this research, the patented innovation data were carefully collected and processed and both the industry-province level and firm level dataset analysed. Using the large and novel panel dataset constructed, both industry level and firm level studies were conducted using the difference-in-differences method (mainly with Poisson regression models) to quantify the policy impacts. In the firm level analyses, the firms with low carbon technologies ("low carbon firms") were matched to a comparable set of control firms without low carbon technologies to understand the differential effects of policies on these firms. Several firm level and industry level variables were also controlled for in the statistical analysis.

The preliminary findings for Singapore indicate that participation in both Kyoto Protocol (1997) and Copenhagen Accord (2009) results in significant increases of 26% and 6% respectively on the development of patented innovations by Singapore's chemical and clean technology firms. The effect of Kyoto Protocol is significantly larger for firms based in Singapore from developed countries than those from developing countries.
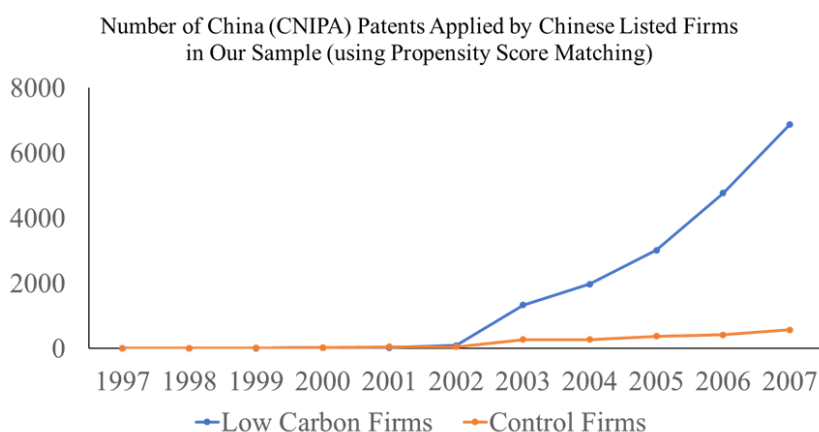
Fig. 5.3: Comparison of number of CNIPA patents applied by Chinese listed firms.

For China, the preliminary findings suggest that the Kyoto Protocol (2002) led to a 2.5 times increase in patented innovations for green IPC (low carbon) sectors in each provincial region in China. Provinces with a less developed technology market have greater effects than provinces with a more developed technology market. Furthermore, it was found that effects for provinces with more developed market intermediaries (e.g., lawyers, accounts and industry organisations) are higher compared with provinces with less developed market inter-

mediaries. Firms in industries from more developed provinces can better enhance their innovation capabilities and increase their innovation output.

These findings advanced the understanding of the impacts of major policies on decarbonisation. Based on the findings, evidence-based recommendations can be proposed for policymakers and firm decision makers on how to better promote the development of decarbonisation technologies and innovation capabilities of firms and industries through sound policy interventions.

Update on work package BB.3
Future roadmap for industrial decarbonisation, including international comparisons

IRP BB continues to work closely with the technology IRPs, including meetings with emerging (and potential) spin-outs from IRP1, IRP2 and IRP3. The novelty of some of the emerging technologies can be challenging to existing industry structures, emphasising the importance of choosing better business models to unlock the value in the technology. Technology and policy reports for the decarbonisation of Singapore as well as the ASEAN region are also being collected in preparation for analysing and gaining insights for regional industrial decarbonisation. In addition to roadmapping, scenario building for Singapore will also be commenced, specifically for chemical industry decarbonisation. IRP BB has also been working separately with the UK government on their roadmaps.

IRP JPS

THE J-PARK SIMULATOR

I RP JPS is an overarching research activity, with the ultimate purpose to show how research coming from each IRP affects the CO_2 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

Over the past six months, the J-Park Simulator (JPS) has progressed on several fronts with regard to enhancing the existing JPS architecture for improved performance and scalability. This step is crucial in order to make use of the full potential of Semantic Web technologies in the JPS. For instance, we have been working on the abstraction and generalisation of JPS agents. An outcome of this task is the design and development of the JPS agent interface and the "JPS agent base" class. The class and all of the agents based on it conform to the interface. With the introduction of this new class, both the logic of the JPS agents as well as the communication between agents become independent of the underlying network protocols. This allows developers to focus solely on the design and development of the agents' internal data processing logic, regardless of the other JPS supporting technologies. We have also developed a generic template to perform listening and responding to HTTP requests, submission and monitoring of jobs to a resource manager system, and managing input and output files associated to a job as well as their transfer between the hardware platforms involved. These generic features are utilised in various agents such as the atmospheric dispersion modelling agent. In addition, we have developed an ontology-based data access (OBDA) project to investigate the possibility of SPARQL queries being executed virtually on any data repositories, e.g. triple stores or data management systems. Furthermore, we have developed a use case by integrating multiples agents into a cross-domain simulation of the atmospheric dispersion of pollutant emissions from a power plant to demonstrate the multi-domain and hierarchical capabilities of the JPS. The use case employs a Density Functional Theory (DFT) agent that performs quantum chemistry calculations at different levels of theories on HPC clusters, an Error-cancelling Balanced Reactions (EBR) agent that produces estimates of standard enthalpy of formation and identifies individual species as either consistent or inconsistent, and a Thermodata agent that calculates the NASA-polynomials with the quantum chemistry calculation of the species as the input.

Moreover, we have constructed an Optimal Power Flow (OPF) model of the UK which consists of 10 regions, to simulate the island of Britain. The regions were based in the regional capitals with an associated load and all the generators within the region (obtained from the Digest of UK Energy Statistics) attached. This model has been utilised to study the effect of carbon tax on decarbonising the energy system and will be expanded upon to include ramp rate, real-time renewable and energy storage system capabilities in the future. We have also integrated a Waste-To-Energy (WTE) decision-support system, developed as part of an Intra-CREATE Seed Collaboration project between National University of Singapore (NUS) and CARES, into JPS. The decision-support system aims to facilitate stakeholders in determining the optimum locations for deploying offsite and onsite facilities for waste management by minimising both the cost of deploying the WTE facilities and the environmental impact that the onsite WTE facilities would impose on the nearby population centres.

Professor Markus Kraft, PI
University of Cambridge
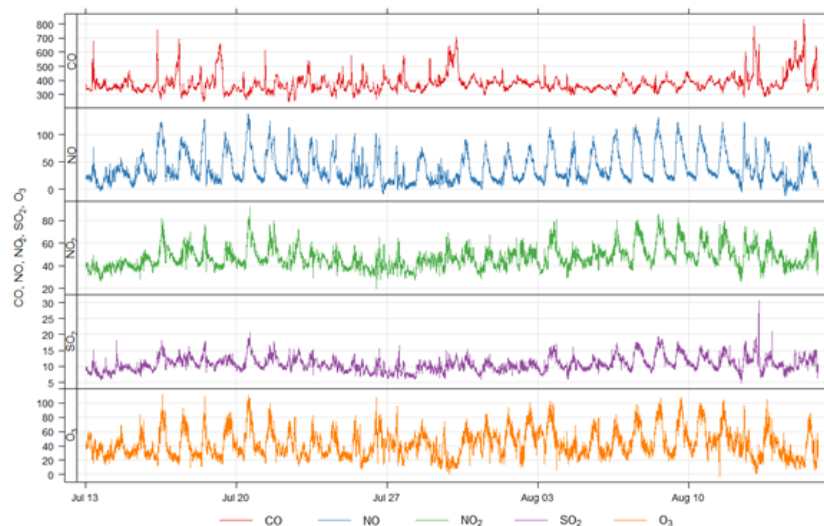
Update on work package JPS.1
Big data — sensors and data modelling

Arkadiusz CHADZYNSKI (Senior Software Developer, CARES), in close collaboration with **Leonardus Kevin ADITYA (Project Officer, NTU)**, has designed and developed the atmospheric dispersion modelling agent for the "virtual sensor" use case by generalising and abstracting multiple required operations for two heterogeneous atmospheric dispersion modelling applications. In particular, the atmospheric dispersion modelling agent can be instantiated as an agent capable of performing atmospheric dispersion modelling either by using the Atmospheric Dispersion Modelling System (ADMS) software (i.e., acting as an existing ADMS agent) or by using the EPISODE software (i.e., configuring itself as an EPISODE agent). This new provision significantly extends the capabilities of JPS, introducing the ability to use computational fluid dynamics simulations for considerably larger spatial scales and with lesser computational resources. In addition, Arkadiusz Chadzynski and Kevin Aditya have integrated multiple "virtual sensor" components and data repositories into a coherent software project.

Laura ONG (Software Developer, CARES) and Kevin Aditya have implemented new agents for the "virtual sensor" use case. For instance, in collaboration with **Dr Kang PAN (Research Fellow, CARES)** and Arkadiusz Chadzynski, they have developed an interpolation agent by identifying suitable interpolation methods to estimate the

pollutant's concentration value at any specified point from the simulated atmospheric dispersion profiles generated by the atmospheric dispersion modelling agents in order to produce a "virtual sensor". This is achieved by creating a Java wrapper for the interpolation model, which tests the inputs for validity and suitability before executing the model. Laura Ong, together with **Dr Yi-chen ZONG (Research Fellow, NUS)**, has developed an "AQMesh" agent to retrieve and store AQMesh's measurement data in both comma-separated values (CSV) and Web Ontology Language (OWL) formats. AQMesh is a small-sensor air quality monitoring system located at the CREATE Tower that offers real-time localised outdoor weather and air quality information accessible via an API in a JavaScript Object Notation (JSON) format. Currently, AQMesh's measurement data for the last 48 hours are stored as a time-series in the knowledge graph while the measurement data for the last one month are stored in a CSV format. In addition, Laura Ong has developed several agents to retrieve real-time air quality and weather data e.g. solar irradiance, local temperature and wind speed, from various external APIs in order to create virtual air quality and weather stations in the knowledge graph. These virtual weather and air quality stations are utilised in multiple use cases such as the Virtual Sensor project, Energy Demand Side Management Framework and Semakau Island Smart Grid project.

Fig. 6.1: AQMesh's measurement data.

Update on work package JPS.2
Surrogate models and superstructure

Arkadiusz CHADZYNSKI (Senior Software Developer, CARES) has been involved in driving forward the overall JPS architecture. For instance, Arkadiusz Chadzynski has been working on the abstraction and generalisation of JPS agents. An outcome of this task is the design and development of the JPS agent interface and the "JPS agent base" class. The class and all of the agents based on it conform to the interface. With the introduction of this new class, both the logic of the JPS agents as well as the communication between agents become independent of the underlying network protocols. This allows developers to fo-

cus solely on the design and development of the agents' internal data processing logic, regardless of the other JPS supporting technologies. Figure 6.2 illustrates the abstraction of the Java Servlet as well as the HTTP protocol technologies. Arkadiusz Chadzynski, in close collaboration with **Dr Feroz FARAZI (Research Associate, CAM)** and **Leonardus Kevin ADITYA (Project Officer, NTU)**, have transferred various generic features, such as submission and monitoring of jobs to a resource manager (e.g. SLURM) on an HPC system, into the JPS Base Library. These generic features are utilised in various agents such as the
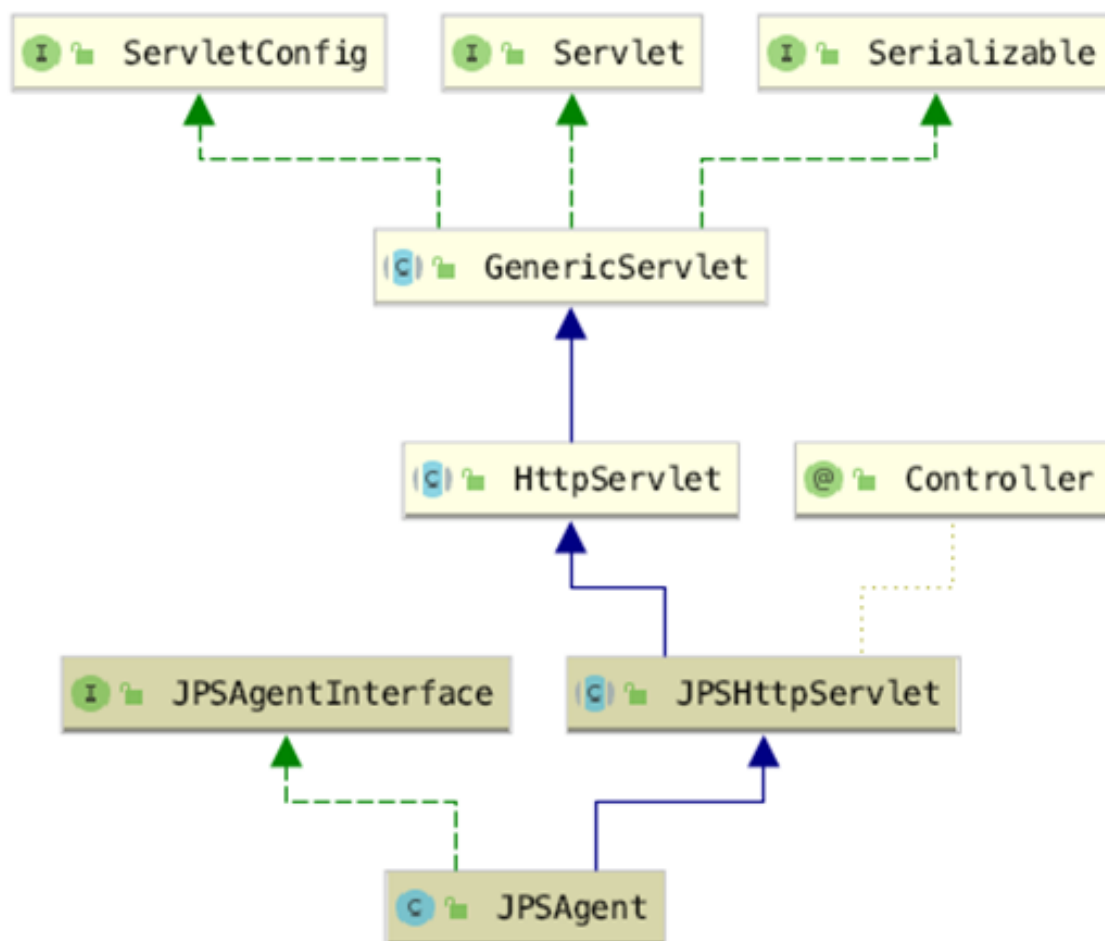

Fig. 6.2: Class diagram for independent JPS Agent design — abstraction of the Java Servlet as well as the HTTP protocol technologies.

atmospheric dispersion modelling agent. Arkadiusz Chadzynski and Dr Feroz Farazi have also further reviewed the existing JPS Base Library to create plans for developing general knowledge-base access components. In particular, the usage of the Java Database Connectivity APIs has been identified as a next step towards generalising how agents interact within the JPS knowledge graph. This new feature will allow JPS to utilise additional computational resources, if necessary. Arkadiusz Chadzynski is also heavily involved in supporting and providing guidance to the JPS team concerning documentation, questions on software design, agent development and non-functional requirements such as performance and scalability. In addition, he is in the process of re-searching potential physical hardware infrastructure upgrades to meet the new requirements effectively and efficiently as JPS progresses.

Laura ONG (Software Developer, CARES) supported Arkadiusz Chadzynski in developing the overall JPS architecture by extending the existing scenario agent. With an increasing number of scenarios being hosted by the JPS, it is necessary to provide unique ID to each scenario in order to avoid any overwriting. Figure 6.3 illustrates this functionality extension. Laura Ong has also improved the performance of the JPS libraries by implementing validation for the information exchanged between agents, enhancing the ability of the JPS libraries for local deployment, as well as refactoring and packaging the pre-existing codes as agents that can apply the semantic web stack to read and understand information from the knowledge graph and modify its data values and/or structure. The agents can now communicate with each other and exchange information via the knowledge graph and semantic input and output parameters.
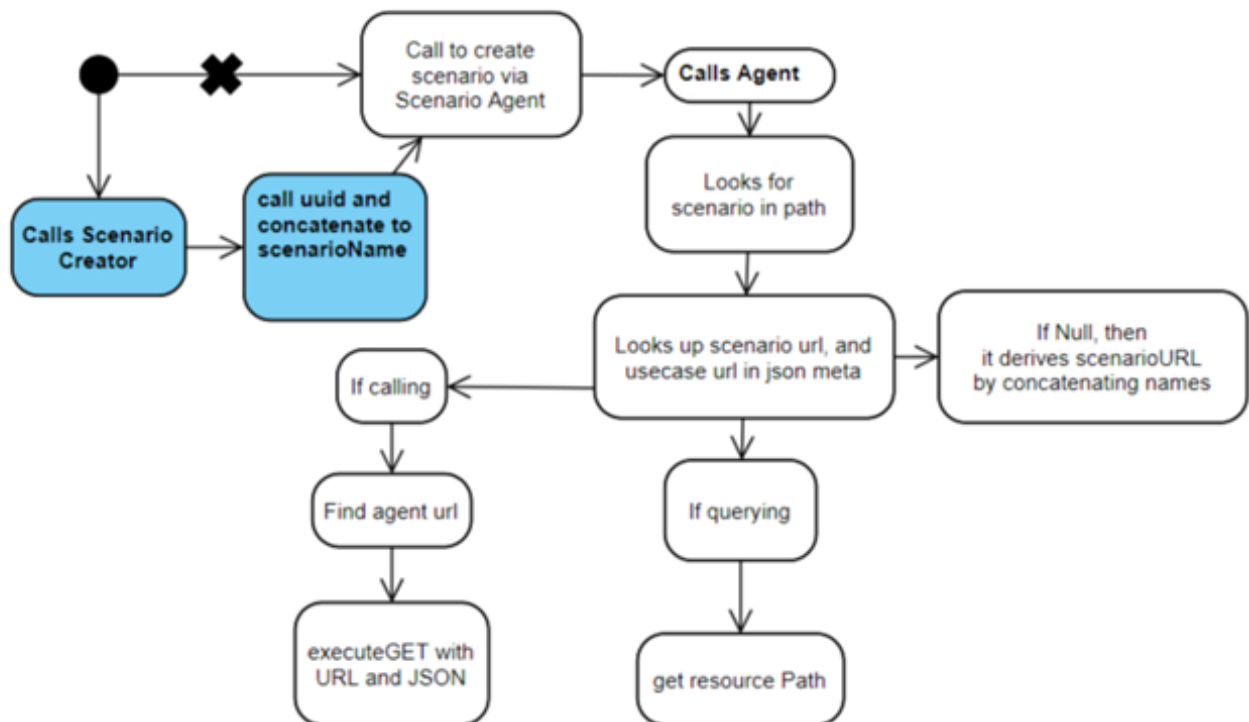

Fig. 6.3: Extension of the scenario creation process — blue boxes denote the addition while the cross-out symbol denotes the obsolete sequence.

Update on work package JPS.3
Implementation

Dr Jethro AKROYD (Senior Research Fellow, CARES), Dr Sebastian MOSBACH (Senior Research Fellow, CARES), Dr Feroz Farazi (Research Associate, CAM) and Angiras MENON (PhD student, CAM) have developed an agent called Density Functional Theory (DFT) Agent to perform quantum chemistry calculations at different levels of theorY on High Performance Computing (HPC) clusters such as the Cambridge Service for Data-Driven Discovery (CSD3). The agent consists of an HTTP request and response component, an asynchronous watcher and a post-processing component. A quantum chemistry calculation job is set up by issuing an HTTP request with parameters that

specify the inputs mainly in the form of Internationalised Resource Identifiers (IRIs), which indicate the locations of input data that are represented in the JPS knowledge graph using the OntoSpecies, OntoCompChem, OntoKin and OntoAgent ontologies. The asynchronous watcher periodically monitors jobs in the agent workspace and submits the jobs (which have been set up, but not started yet), checks the status of running jobs for successful completion, transfers the completed jobs' results from the HPC cluster to the machine where the agent is being executed and processes the results to upload the calculated thermodata into the knowledge graph.
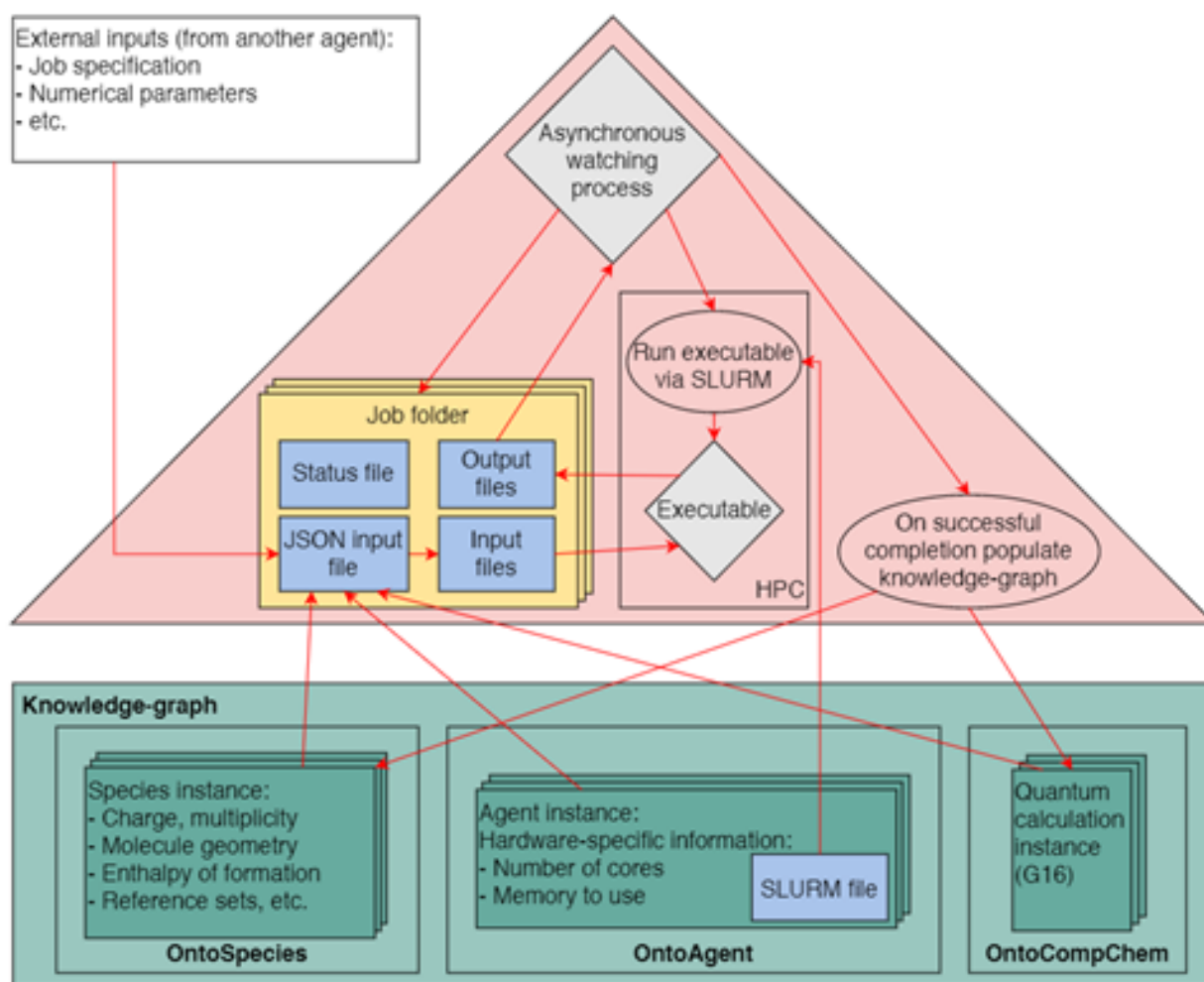

Fig. 6.4: Elements of a generic agent (red triangle) and how they interact with the knowledge graph (green box). An asynchronous watcher (grey diamond) manages running an executable (grey diamond), with all associated input and output files (blue boxes).
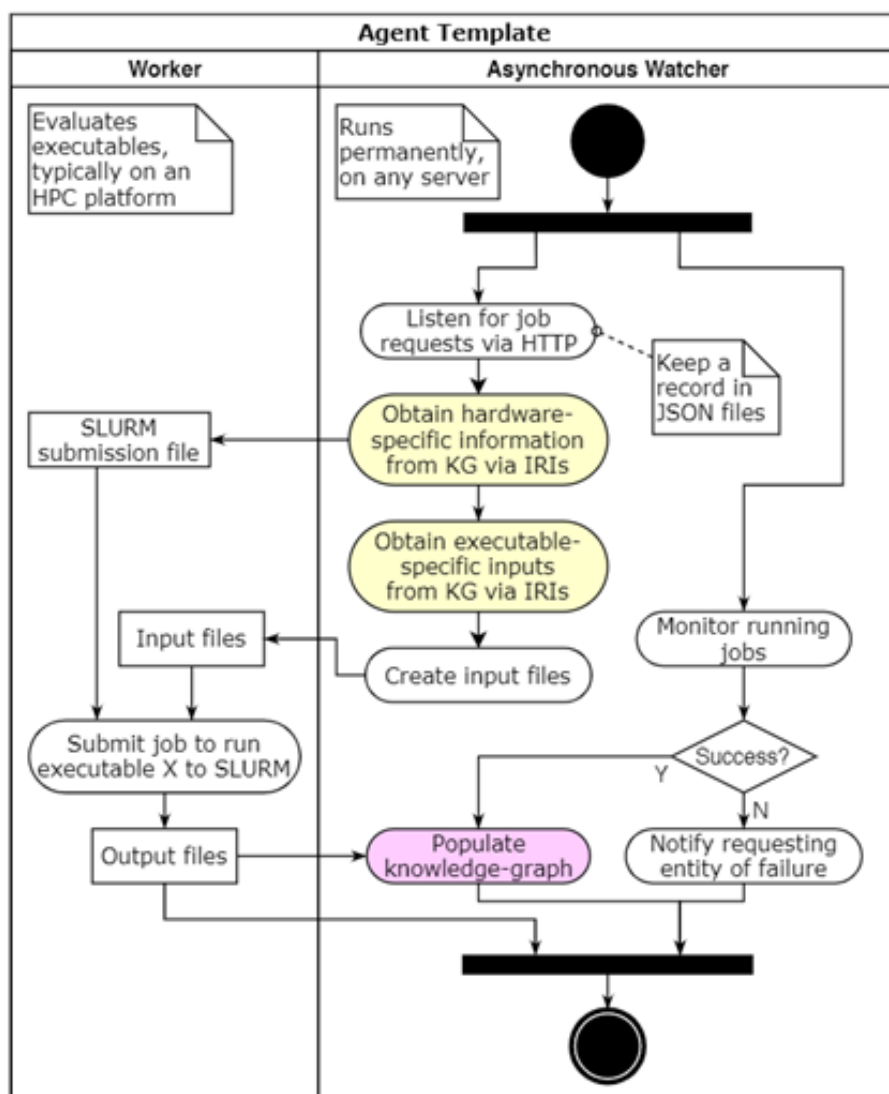
Fig. 6.5: UML activity diagram of a generic agent which enables computational jobs to be executed asynchronously on an HPC system upon HTTP request, with inputs obtained from the knowledge graph (shaded in yellow) and outputs written back into the knowledge graph (shaded in magenta).

A Thermodata Agent has been employed in calculating the NASA-polynomials with the quantum chemistry calculation of the species as the input. For each calculation of a species, the DFT Agent represents the Gaussian log file in the knowledge graph using the OntoCompChem ontology. The agent also updates the NASA-polynomials in all chemical kinetic reaction mechanisms containing the species. This work is motivated by the fact that currently, a major barrier to using chemical models in an Industry 4.0 environment is the significant inconsistency between chemical kinetic reaction mechanisms, both in terms of naming of chemical species and in terms of thermodynamic, kinetic and transport data. The inherent complexity of chemical kinetic reaction mechanisms and the inconsistency challenges render it infeasible to solve these problems manually. Instead, a systematic and automated approach is required.

While developing agents for various tasks, it became clear that many design features are entirely generic, i.e. independent of the specific task. Such design features include, most importantly, listening and responding to HTTP requests, submission and monitoring of jobs to a resource manager (e.g. SLURM) on an HPC system and managing input and output files associated to a job as well as their transfer between the hardware platforms involved. A template has thus been developed that is, within reason, applicable to 'any' (Linux) executable (Figures 6.4 and 6.5).

Dr Nenad B. KRDZAVAC (Senior Software Developer, CARES) together with Dr Feroz Farazi, Dr Sebastian Mosbach, Dr Jethro Akroyd and Angiras Menon have developed an Error-cancelling Balanced Reactions (EBR) Agent. The purpose of this agent is two-fold. Given a set of chemical species, it can produce estimates of standard enthalpy of formation, and in addition, within the given set, identify individual species as either consistent or inconsistent. The agent operates in two steps. The first step computes the standard enthalpy of formation of a species using EBRs. At the centre of this method lies Hess's law, which states that the total enthalpy change of a reaction is equal to the sum of all individual enthalpy changes, independent of the reaction pathway. The reaction enthalpy can thus be estimated from the results of quantum chemistry calculations.

However, it is known that estimating enthalpies using quantum chemical calculations results in systematic errors. To circumvent this, EBRs, which make use of structural and electronic similarities between the species in a reaction to allow cancellation of the systematic errors are employed. Examples of types of EBRs include isogyric reactions, which conserve the number of spin states during the reaction, and isodesmic reactions, which conserve the number of each type of bond during the reaction. Using EBRs enables improved estimates of standard enthalpies of formation of species from quantum chemical calculations.

The second step performed by the agent is a heuristic cross-validation. A set of species is given to the agent, each with a reference value for the standard enthalpy of formation. These reference values may be derived experimentally or from high-level computational methods. Next, one species in the set is selected, in a leave-one-out cross-validation method. For the selected species, a user-defined number of EBRs are generated. Each EBR can then be used to estimate the standard enthalpy of formation of the species. For each EBR, the estimated standard enthalpy of formation generated for the species is then compared to the reference value, and an error is computed. The EBR is accepted if this error is below a defined upper limit, and rejected otherwise. If all EBRs for a given species are rejected, the species is flagged as potentially inconsistent. This process is repeated for all of the species in the reference set to categorise them as consistent or potentially inconsistent.

The set of consistent and potentially inconsistent species is then refined by selecting the potentially inconsistent species with the highest average error and generating a new set of EBRs for it using only species that were deemed consistent in the initial sorting. The errors are then recomputed for this new set of EBRs. If the average error for the new set of EBRs is lower than the error for the initial set of EBRs, then it is assumed that the original inconsistency for this species is due to another species that appeared in the original EBRs, and the selected species is added to the consistent set. The process is repeated for each potentially inconsistent species in descending order of average error until the set of inconsistent species does not change. At this point, convergence is reached, and the set of inconsistent species is reported as requiring an improved estimate of the standard enthalpy of formation. It is noted that, depending on the size of the species set and other parameters, executing the algorithm can be computationally expensive.

(a) CO emissions predicted using the original mechanism.

(b) CO emissions predicted using a mechanism with updated thermodata.
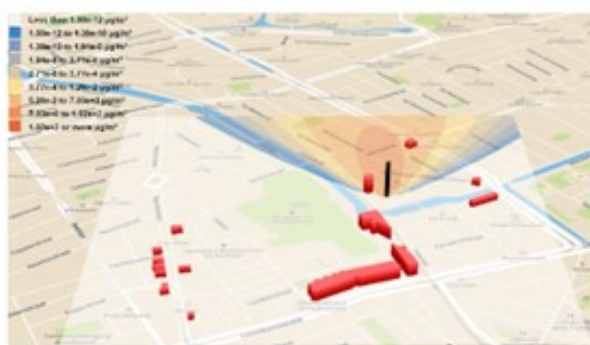
(c) uHC emissions predicted using the original mechanism.

(d) uHC emissions predicted using a mechanism with updated thermodata.

Fig. 6.6: Screenshots of a web-interface showing pollutant concentration distributions in the atmosphere over The Hague as predicted by ADMS, with 3D-representation of selected buildings.

The design and implementation of this EBR agent follows the generic template as shown in Figure 6.4. Setting up an EBR job requires a number of inputs including a list of pairs of IRIs for target and reference species, number of iterative calculations or runs, number of radicals and number of reactions. Each pair consists of an IRI to a unique species instance in OntoSpecies and an IRI to a quantum calculation in OntoCompChem. Once all inputs are retrieved via queries developed in SPARQL, a SPARQL Protocol and RDF Query Language, from the JPS knowledge graph, a job is created in the agent workspace and then submitted by the asynchronous watcher to the HPC cluster. Following the successful completion of jobs, results are uploaded into the JPS knowledge graph.

A use case has been developed by integrating the DFT, EBR and Thermodata agents into a cross-domain simulation of the atmospheric dispersion of pollutant emissions from a power plant and displaying this interactively on a webpage (Fig. 6.6). Three-dimensional representations of selected buildings are included, which are stored in the knowledge graph using the OntoCityGML ontology. The atmospheric dispersion of pollutants is simulated using the Atmospheric Dispersion Modelling System (ADMS), which is based on a fluid-dynamic model that includes Gaussian plume air dispersion. ADMS requires as one of its inputs, weather data, which are retrieved in real-time from the World Wide Web and stored in the knowledge graph by a dedicated weather agent. All relevant data are held in the knowledge graph and as such are linked through IRIs.

Dr Nenad Krdzavac, together with Dr Feroz Farazi, Dr Sebastian Mosbach and Dr Jethro Akroyd, has implemented an agent to monitor the status of the JPS knowledge graph (Figure 6.7). The agent counts the number of instances of selected species and reactions within the OntoSpecies, OntoKin and OntoCompChem ontologies. A time-history chart of species (Figure 6.8) in the chemical kinetic reaction mechanisms, which are represented in the knowledge graph using OntoKin, is visualised. Dr Nenad Krdzavac is also involved in the development of a parser that extracts data from Gaussian log files and generates OWL files. The parser has been embedded into the JPS and can be used for uploading data into the JPS knowledge graph.

Dr Jethro Akroyd, Dr Sebastian Mosbach, Dr Nenad Krdzavac and Dr Feroz Farazi have developed an ontology-based data access (OBDA) project to investigate the possibility of SPARQL queries being executed virtually on any data repositories, e.g. triple stores or data management systems. An open-source API called Ontop, which is scalable up to tens of millions of triples, is used to set up the type of OBDA required to be integrated into the JPS. OBDA is built around W3C recommended standards, for example, the expressivity of ontology whose classes and properties will be referred from SPARQL queries (https://www.w3.org/TR/rdf-sparql-query/) should remain in OWL 2 QL (https://www.w3.org/TR/owl2-profiles) and the mapping between a relational database and the ontology is defined in R2RML (https://www.w3.org/TR/r2rml/). The Protege plugin of Ontop provides easy connectivity between the ontology and data management systems. Ontop has built-in support for major data storage systems including PostgreSQL, Oracle, IBM DB2, SQL Server and MySQL.
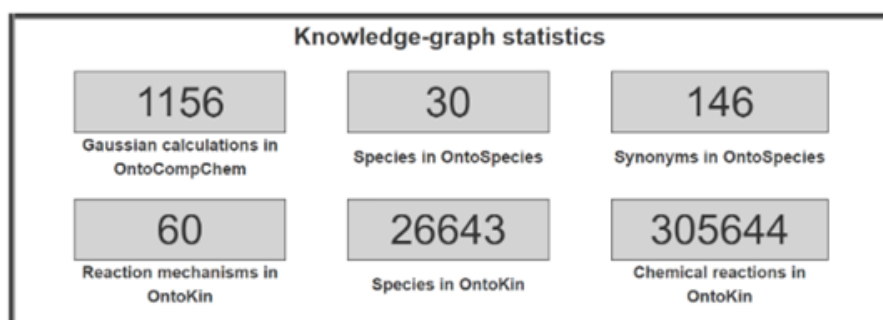

Fig. 6.7: Counters of selected concepts, including quantum calculations, unique species, mechanisms, species, and reactions.
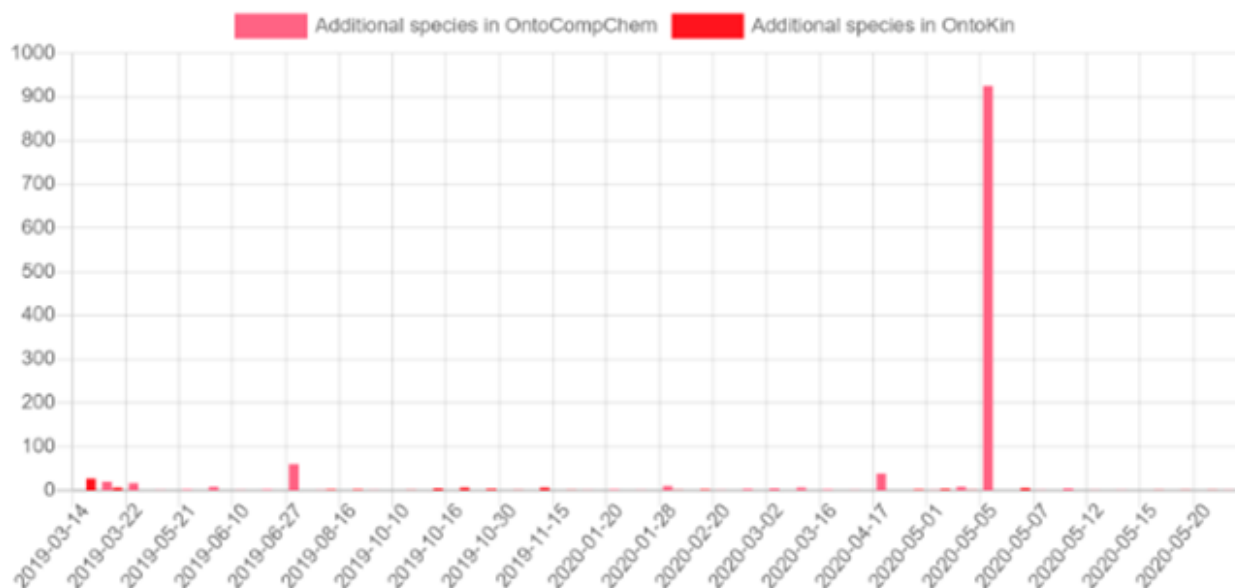

Fig. 6.8: Time-history chart showing numbers of species added on particular dates.

Aravind DEVANAND (Research Associate, CARES), Gourab KARMAKAR (Research Engineer, CARES) and Dr Nenad Krdzavac have been involved in the development of the ElChemo framework. The framework has been applied to investigate the cross-domain interactions between the chemical and electrical domains of a depropaniser section that have been modelled using gPROMS and MATLAB respectively. They have developed a rule-based system using SPARQL Inferencing Notation (SPIN) to ensure smooth operation of the plant and to detect any deviation from standard operation. The SPIN agent checks for any constraint violation in the outputs of both gPROMS and MATLAB agents. Figure 6.9 illustrates the implementation of the constraint violations in the "TopBraid Composer" environment for the depropaniser. The rules dictate that there is a unique value for the mole fraction of isobutane (propane) in the

bottom of the depropaniser (distillate) and that the value must not be less than 0.973. In addition, the sum of the mole fraction of all the components in a process stream (bottom or distillate) must be equal to 1. Before storing the gPROMS agent's outputs, e.g. composition of distillate and bottom into the knowledge graph, a consistency checking agent that uses the HermiT Reasoner is employed to determine the consistency of the provided logical axioms. Rules are also implemented in a similar way to detect any power quality constraint violation in the electrical domain. They are in the process of implementing the SPIN constraints in Java and packaging the models as agents that can apply the semantic web stack to read and understand information from the knowledge graph and modify its data values. They are also involved in preparing a paper, titled "ElChemo: A Cross-Domain Interoperability in a Chemical Plant" which describes the main

Fig. 6.9: Implementation of the constraint violations using SPIN in the "TopBraid Composer" environment for the depropaniser - mole fraction of isobutane (propane) in the depropaniser's bottom (distillate).

ideas and results of this work. Gourab Karmakar is also involved in the supervision of **Bryan LEE Zhen Yuan (Intern, NTU)**, who is developing a model to generate the electrical engine's reactive power profile based on the active power profile obtained from the gPROMS agent.

Gourab Karmakar has been working on integrating an energy demand side management framework, developed as part of an Intra-CREATE Seed Collaboration project between NUS and CARES, into JPS. He has further extended the domain ontology for power systems, OntoPowSys, to describe the relevant technologies, prosumers, electrical and energy components etc. utilised in the framework. Instances of the relevant technologies, prosumers, electrical and energy components etc. have been created and incorporated into the JPS knowledge graph. Gourab Karmakar , in close collaboration with the NUS team, is working on modularising the model to improve its scalability.

Laura ONG (Software Developer, CARES) and Leonardus Kevin ADITYA (Project Officer, NTU) have integrated a Waste-To-Energy (WTE) decision-support system, developed as part of an Intra-CREATE Seed Collaboration project between NUS and CARES, into JPS by using the "parallel world" framework. The decision-support system aims to facilitate stakeholders in determining the optimum locations for deploying offsite and onsite facilities for waste management. The system consists of a bi-objective robust optimisation model—to minimise both the cost of deploying the WTE facilities and the environmental impact that the onsite WTE facilities would impose on the nearby population centres. This system has been applied to create a use case to study food waste disposal in Singapore. In this use case, 109 food courts distributed across the entire Singapore were selected and instantiated in the knowledge graph, along with their corresponding location and level of waste production.
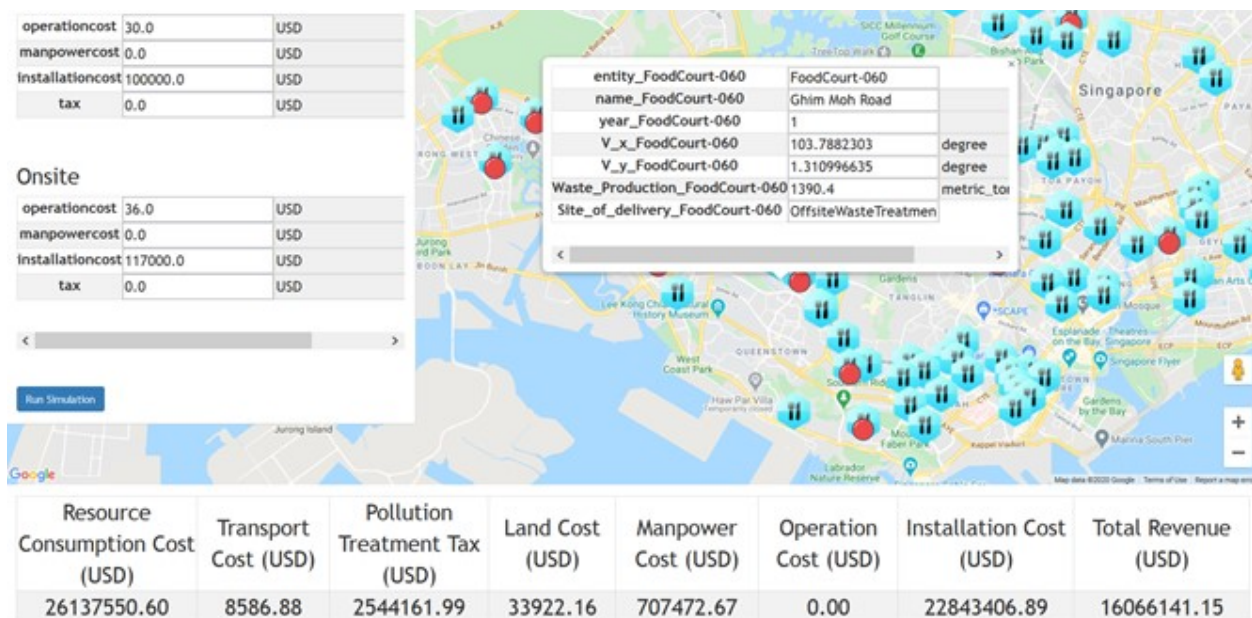
Fig. 6.10: Visualisation of the Waste-To-Energy (WTE) decision-support system. The red circles denote the onsite clusters, while the blue hexagons denote the waste generation sites. The costs associated with the scenario are reflected in the table.

Three offsite WTE facilities were selected to represent the decentralised treatment capabilities. Laura Ong has also developed a visualisation for displaying the locations of the waste generation sites as well as the optimum locations for deploying offsite and onsite WTE facilities. Upon clicking on the icon, a pop-up window containing the information about the selected component will appear. By varying the number of clusters as well as various types of cost, different scenarios can be created which allow the impact on the revenue, economic costs and number of onsite WTE facilities to be studied. In addition, as the system estimates the level of waste production over a period of 15 years, the impact of increasing level of waste production on the optimum locations for waste disposal can also be investigated.

Laura Ong has also been working on improving the modularity of the energy storage technology decision-making use case, in order to consider more types of energy storage systems. In addition, she introduced alternative pathways to handle non-convergence of the Optimal Power Flow (OPF) simulation, i.e. an error is thrown to the user instead of storing the invalid outputs into the knowledge graph.

John ATHERTON (PhD student, CAM) has constructed an OPF model of the UK which consists of 10 regions, to simulate Great Britain. The regions were based in the regional capitals with an associated load and all the generators within the region (obtained from the Digest of UK Energy Statistics) attached. The 10 buses corresponding to the 10 regions were connected with averaged direct transmission overhead lines. Using this model, it was observed that as the carbon tax increases, the coal power plants were replaced with Combined Cycle Gas Turbine (CCGT) power plants. The most significant rate of change occurs when the carbon tax is high enough such that it is cheaper to use gas than coal for power production on the generator side. However, due to the inclusion of transmission losses and that gas is typically found closer to the larger southern loads, gas is phased in earlier when using a regional model compared to an aggregated national model. This is because the transmission losses work alongside the carbon tax in incentivising the replacement of northern coal with southern gas to meet the southern loads. This model will be expanded upon to include ramp rate, real-time renewable and energy storage system capabilities.
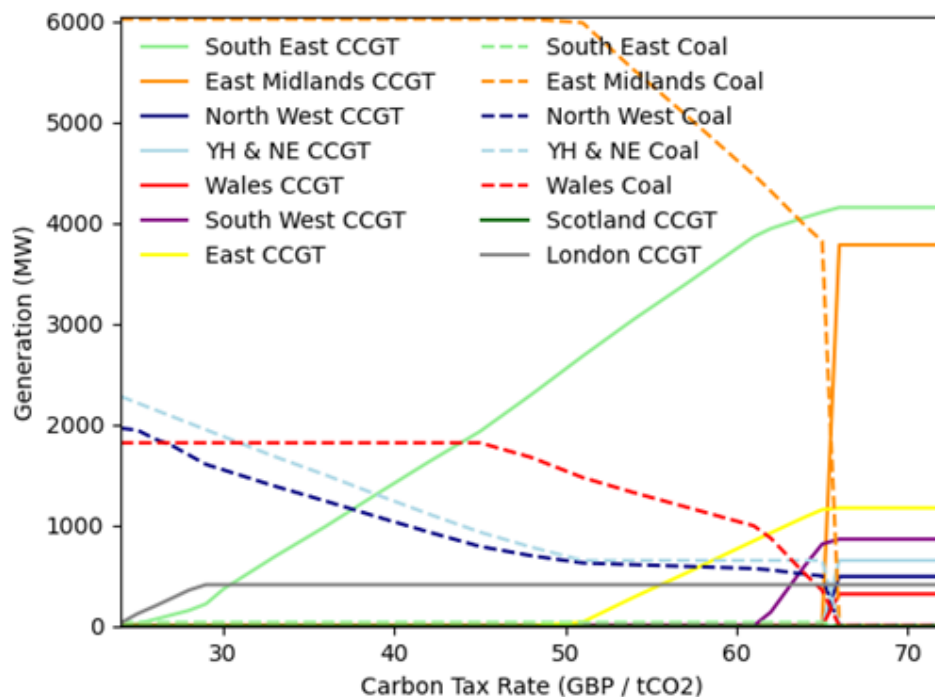
Fig. 6.11: Coal and CCGT power generation levels by region in Great Britain. Each region is represented by a colour; with CCGT being denoted by solid lines and coal being denoted by dashed lines.

Wanni XIE (in-kind PhD student, CAM) has utilised the existing domain ontology for power systems, OntoPowSys, to create a knowledge graph for the UK energy system by semantically describing the grid topology, technical data of the buses, branches and generators for the above-mentioned 10-buses grid model of the UK. Wanni Xie has packaged the model as an agent. She has also augmented the existing UK power plant instances by consolidating the data from different data sources and by improving the expressiveness of the OntoEIP ontology, which is used to describe the upper-level information of the power plants. The expressiveness of the OntoEIP is enhanced by adding new classes and properties to account for more types of energy source (e.g. wind, solar, biomass) and generation technologies. The two domain ontologies, OntoEIP and OntoPowsys, are employed in instantiating over 1,000 UK power plants. Wanni Xie, in collaboration with Dr Feroz Farazi and **Shaocong ZHANG (Software Developer, CARES)** has developed a visualisation for displaying the UK grid model and power plants (Figure 6.12). Upon clicking on the icon, a pop-up window containing the information about the selected component will appear.
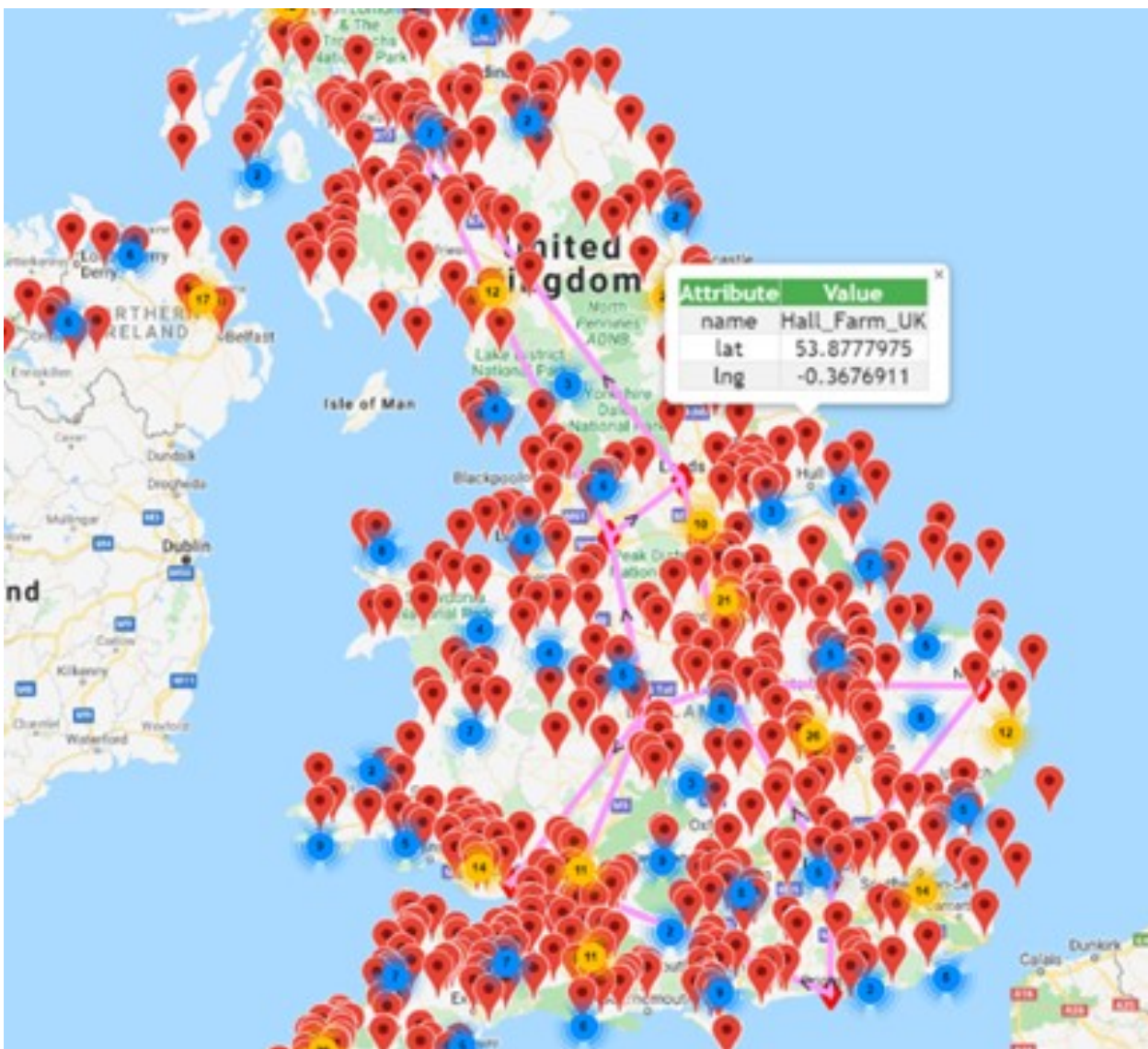
Fig. 6.12: Visualisation of the UK grid model and power plants. The red markers denote power plants, while the yellow and blue circles represent the number of power plants within a local region. The pink lines denote electrical lines and the red diamonds represent the regional-level electrical buses.

Update on work package JPS.4
Model analysis and visualisation

Laura ONG (Software Developer, CARES) has developed a visualisation for displaying the atmospheric dispersion profiles generated by the EPISODE and ADMS agents. Using the Google HeatMap library, the visualisation represents pollutants' concentration values as varying degrees of hue and intensity. A legend was created using the D3 library to indicate the range of concentration values for each pollutant. The visualisation also consists of markers denoting the locations of ships and sensors. Upon clicking on the

sensor icon, a table will be generated – displaying the pollutants' concentration values, their mean, minimum and maximum values as well as the Pollutant Standards Index (PSI). The user can modify the area of interest and type of pollutant by selecting from the dropdown list. A slider was customised via Bootstrap to allow the selection of atmospheric dispersion profiles corresponding to different heights above the sea level.

Fig. 6.13: Visualisation of the atmospheric dispersion profiles (pollutants' concentration values) generated by the EPISODE agent at a height of 30 metres above the sea level. Red denotes areas with high pollutant's concentration values while green denotes areas with low pollutant's concentration values.

pollutant	concentration	time	allpsi	mean	max	min	individualpsi
SGAQMeshCO2Sensor-001	770390.00 ug_per_m.m.m	2020-09-07T14:00:00+08:00	54	768896.25 ug_per_m.m.m	855100.00 ug_per_m.m.m	716090.00 ug_per_m.m.m	0.00
SGAQMeshCOSensor-001	335.18 ug_per_m.m.m	2020-09-07T14:00:00+08:00	54	428.08 ug_per_m.m.m	712.32 ug_per_m.m.m	294.99 ug_per_m.m.m	4.00
SGAQMeshNO2Sensor-001	78.63 ug_per_m.m.m	2020-09-07T14:00:00+08:00	54	72.82 ug_per_m.m.m	80.35 ug_per_m.m.m	55.08 ug_per_m.m.m	0.00
SGAQMeshNOSensor-001	101.60 ug_per_m.m.m	2020-09-07T14:00:00+08:00	54	97.80 ug_per_m.m.m	103.79 ug_per_m.m.m	93.11 ug_per_m.m.m	0.00
SGAQMeshNOxSensor-001	180.23 ug_per_m.m.m	2020-09-07T14:00:00+08:00	54	172.87 ug_per_m.m.m	180.23 ug_per_m.m.m	166.07 ug_per_m.m.m	0.00
SGAQMeshO3Sensor-001	57.84 ug_per_m.m.m	2020-09-07T14:00:00+08:00	54	29.56 ug_per_m.m.m	94.24 ug_per_m.m.m	0.00 ug_per_m.m.m	13.00
SGAQMeshPM10Sensor-001	43.63 ug_per_m.m.m	2020-09-07T14:00:00+08:00	54	36.34 ug_per_m.m.m	66.40 ug_per_m.m.m	15.81 ug_per_m.m.m	36.00
SGAQMeshPM1Sensor-001	5.86 ug_per_m.m.m	2020-09-07T14:00:00+08:00	54	4.85 ug_per_m.m.m	8.99 ug_per_m.m.m	2.16 ug_per_m.m.m	0.00

Shaocong ZHANG (Software Developer, CARES) has applied her previous work (a prototype of an ontology matching framework that performs data consolidation by taking advantage of JPS's multi-level and multi-domain design for terminology definition) to conduct matching for power plant instances from DBPedia and JPS. In order to achieve this, she has refactored and packaged the prototype as six different agents that can apply the semantic web stack to read and understand information from the knowledge graph and modify its data values and structure. The six agents are: 1) Lexical processor agent—extracts the lexical information from the ontology file; 2) Element-level matcher (ELM) agent— performs element-level ontology matching using designated dimensions e.g. 'value', 'string'; 3) Aggregator agent—consolidates the matching results from various ELM using weighted sum, cardinality or class constraint; 4) Topic model agent—performs topic modelling which is used by 'domain' type ELM agent to determine the semantic distance between two potential entities; 5) Data linking agent—performs data linking between a pair of identified matching instances; and 6) Coordination agent—coordinates the involved agents to fulfil the prototype's objectives.

Table 12: *Instance Alignment on Germany Dataset: false positive marked with #.*

source entity	target entity	score
dbp:Neurath_Power_Station	jps:Neurath_Coal_Power_Plant_Germany	0.628
# dbp:Hesselbach_Wind_Farm	jps:Voerde_Coal_Power_Plant_Germany	0.623
dbp:Heilbronn_Power_Station	jps:Heilbronn_Coal_CHP_Power_Plant_Germany	0.637
dbp:Schwarze_Pumpe_power_station	jps:Schwarze_Pumpe_Coal_Power_Plant_Germany	0.735
dbp:Werdohl-Elverlingsen_Power_Station	jps:Werdohl-Elverlingsen_E_CCGT_Power_Plant_Germany	0.635
dbp:Wilhelmshaven_Power_Station_(E.ON)	jps:Wilhelmshaven_Coal_Power_Plant_Germany	0.655
dbp:Jänschwalde_Power_Station	jps:Janschwalde_Coal_Power_Plant_Germany	0.621
dbp:Rostock_Power_Station	jps:Rostock_CHP_Coal_Power_Plant_Germany	0.708
dbp:Niederaussem_Power_Station	jps:Niederaussem_Coal_Power_Plant_Germany	0.658
dbp:Frimmersdorf_Power_Station	jps:Frimmersdorf_Coal_Power_Plant_Germany	0.722
dbp:Altbach_Power_Station	jps:Altbach_Coal_Power_Plant_Germany	0.709
dbp:Bexbach_Power_Station	jps:Bexbach_Coal_CHP_Power_Plant_Germany	0.697
dbp:Lippendorf__Kraftwerk__1	jps:Lippendorf_Coal_Power_Plant_Germany	0.714

Fig. 6.14: Alignment of power plant instances for Germany from DBPedia and JPS.

Xiaochi ZHOU (PhD student, CAM) has designed and implemented a novel Question Answering (QA) system for chemical data in the JPS knowledge graph. This QA system can answer a range of questions as shown in Figure 6.15. Using the user-provided question as an input, the QA system converts it into SPARQL queries which are sent to the JPS knowledge graph to retrieve data from chemistry-related ontologies including OntoKin (for chemical kinetic reaction mechanisms), OntoSpecies (for chemical species) and OntoCompChem (for quantum chemistry calculations). The QA system also queries the Wikidata knowledge graph, which provides information about the basic physical and chemical properties of chemical substances. The QA system is built upon a wide range of Natural Language Processing tools, including Named Entity Recognition (NER), neural network-based text embedding, and topic modelling. The workflow of the

Sample questions	**ontology**
1. what are the acidity of all carboxylic acid	Wikidata
2. what are the boiling points of all alkanol	Wikidata
3. what are the structures all aromatic hydrocarbon	Wikidata
4. species with an molecular weight larger than 200	Wikidata
5. what reaction has CH4 as reactant	JPS
6. what mechanism contains CH4 + OH	JPS
7. what is the reaction rate for CH4 + OH	JPS
8. what is the product of H2 + OH	JPS
9. is the reaction H + H2O => H2 + OH reversible	JPS
10. what reactions produce NO2 + O2	JPS

Fig. 6.15: Examples of questions (in a human-readable format) processed by the QA system.

QA system is shown in Figure 6.16. The QA system first uses NER to identify the key components in the question posed by the user – in a human-readable format e.g. "What is the boiling point of Benzene", and categorise them accordingly. In this specific example, "boiling point" and "Benzene" will be identified as the key components and classified as the type "attribute" and "entity" respectively. The QA system will then map the key components to their corresponding semantic representations in the form of Uniform Resource Identifiers (URIs). When ranking the URIs returned from performing ontology lookup, the QA system not only considers the string similarity between the natural language labels of the URIs and the key components, it also leverages the Latent Dirichlet Allocation (LDA) topic model to identify the affiliation between the ontology and the components. The inclusion of the LDA topic model increases the accuracy of the ontology lookup process as the QA system can now differentiate similar concepts, relations, or entities from different ontologies. In addition, the QA system utilises the Rasa framework, which is an open-source AI framework for constructing contextual assistants, to classify the questions in order to map them to their corresponding SPARQL query templates. Using the URIs of the key components, the QA system constructs SPARQL queries by populating the SPARQL query templates. Subsequently, the SPARQL queries are sent to the SPARQL endpoints in the JPS knowledge graph to retrieve the data.

Fig. 6.16: Workflow of the QA system.
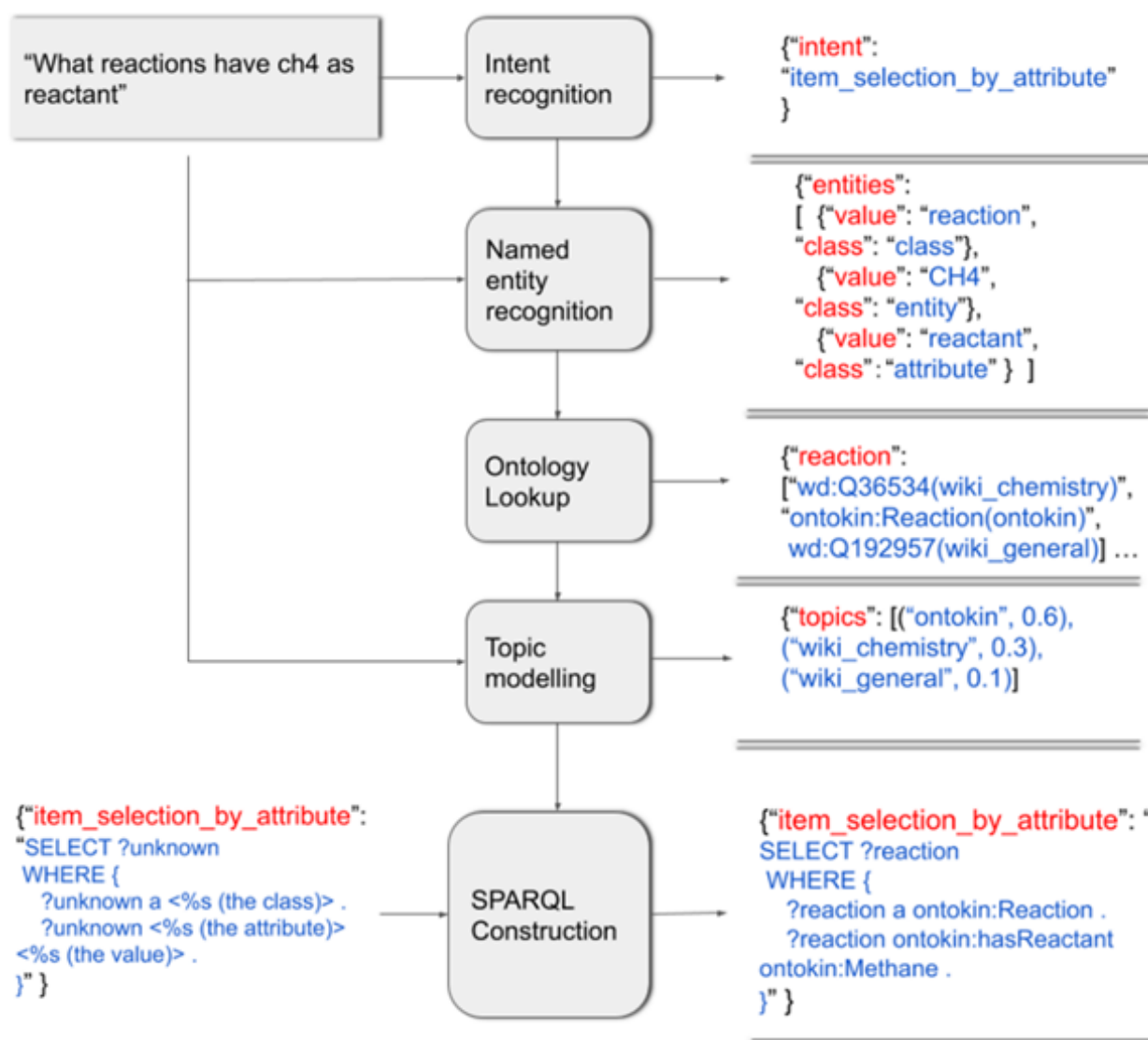
Scientific output

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 17.

Deep kernel learning approach to engine emissions modelling

Changmin Yu, Marko Seslija, George Brownbridge, Sebastian Mosbach, Markus Kraft, Mohammad Parsi, Mark Davis, Vivian Page, and Amit Bhave, *Data-Centric Engineering*

Abstract: We apply deep kernel learning (DKL), which can be viewed as a combination of a Gaussian process (GP) and a deep neural network (DNN), to compression ignition engine emissions and compare its performance to a selection of other surrogate models on the same dataset. Surrogate models are a class of computationally cheaper alternatives to physics-based models. High-dimensional model representation (HDMR) is also briefly discussed and acts as a benchmark model for comparison. We apply the considered methods to a dataset, which was obtained from a compression ignition engine and includes as outputs soot and NOx emissions as functions of 14 engine operating condition variables. We combine a quasi-random global search with a conventional grid-optimization method in order to identify suitable values for several DKL hyperparameters, which include network architecture, kernel, and learning parameters. The performance of DKL, HDMR, plain GPs, and plain DNNs is compared in terms of the root mean squared error (RMSE) of the predictions as well as computational expense of training and evaluation. It is shown that DKL performs best in terms of RMSE in the predictions whilst maintaining the computational cost at a reasonable level, and DKL predictions are in good agreement with the experimental emissions data.

Other activities and achievements

Aravind DEVANAND (Research Associate, CARES) and **Gourab KARMAKAR (Research Engineer, CARES)**, under the supervision of **Dr Franziska SIELKER (PI, CAM)**, have developed an Intra-CREATE Seed Collaboration proposal with the Singapore-ETH Centre. The proposal was recently awarded with CARES being the host institution. The proposal, titled "Consumer Energy Usage Data in Smart City Development (CEUS)" addresses the necessity of standardisation in the Singapore's electricity consumer domain and proposes a knowledge-enabled common data-driven platform based on a Common Information Model (CIM). This platform aims to facilitate consumers in analysing their energy usage information, hence encouraging their active participation in the retail energy market which will lead to better informed decision-making. The proposal also aims to identify necessary policies to enable the implementation of a Singapore-wide CIM. Besides providing consumers' energy usage information, the CIM can also contribute to improving the accuracy and efficiency of the planning process for the energy systems.

Aravind DEVANAND is also involved in the supervision of **Benjin LAU (Intern, NTU)**, who is improving the existing carbon tax model employed in the carbon tax use case, in order to consider more types of alternative energy sources as well as the electrical network constraints when determining the optimal configuration for the power generators.

eCO₂EP

CARBON CAPTURE AND UTILISATION USING A TABLE-TOP CHEMICAL FACTORY

This is CARES' first Intra-CREATE project and is aimed at developing a "table-top chemical factory" that uses electrochemical processes to convert CO_2 into ethylene or to 1-propanol – two molecular products widely used in the chemical industry. Earlier research carried out at CREATE had demonstrated that CO_2 molecules can be transformed into hydrocarbons through the application of electro-catalysis. eCO₂EP's research studies the viability of scaling CO_2 reduction processes, including techno-economic evaluation of the use of off-peak renewable electricity in areas with excess capacity, with the goal of developing new energy-chemistry solutions for a more sustainable future.

eCO₂EP Principal Investigators:

Professor Alexei LAPKIN
University of Cambridge

Professor Joel AGER
University of California, Berkeley

OVERVIEW

The time frame covered by this biannual report corresponds to eCO2EP project months 28-33. Significant progress has been made in designing, fabricating and commissioning the table-top CO_2 reduction reactor which is the focus of the project. Key milestones regarding the component specifications have been met, including achievement of >200 mA cm^{-2} current density for the production of ethylene and development of compatible anode materials. Team members have been developing promising approaches for the downstream separation of the products of the table-top reactor. There have been initial discussions with potential industrial collaborators to implement eCO2EP-developed technology into chemical manufacturing plants.

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

Fe-modified Ni foam (10*10 cm²) for CO_2-electrolyzer:

Dr CHEN Yubo (Research Fellow, NTU) and colleagues attempted to increase the catalytic activity of pristine Ni foam for oxygen evolution by modifying the Ni surface with Fe. A Fe-modified Ni foam has been prepared by immersing the Ni foam in a 20 mM iron nitrate solution. An activity improvement of more than one order of magnitude is obtained after the addition Fe-modification.

Dr LIU Guanyu (Research Fellow, NTU) has been investigating the influence of roughness factor and oxidation state on the selectivity of copper-based electrocatalysts for carbon dioxide reduction. It was found that the Cu catalyst with a medium roughness factor showed the highest Faradaic efficiency towards C2+ products. Furthermore, oxidation states of Cu-based electrocatalysts played a more important role than roughness factors for selectivity towards C2+ production. He has also been developing 2D copper-based catalysts for highly selective ethylene and ethanol production enabled by nano-defects, which are examined by both H-cell and flow cell. Dr Liu Guanyu submitted a manuscript entitled "Photoelectrochemical CO_2 Reduction on InP Nanopillar-Array Photocathodes with Au-TiO$_2$ Interface for Tunable Syngas Production" to a scientific journal with Prof. Joel W. Ager, Prof. Xu Rong and Prof. Markus Kraft, as well as a book chapter about electrocatalytic oxygen evolution reaction for book entitled "Photo- and Electro-Catalytic Processes: Water Splitting, N_2 Fixing, CO_2 Reduction" with Prof. Joel W. Ager.
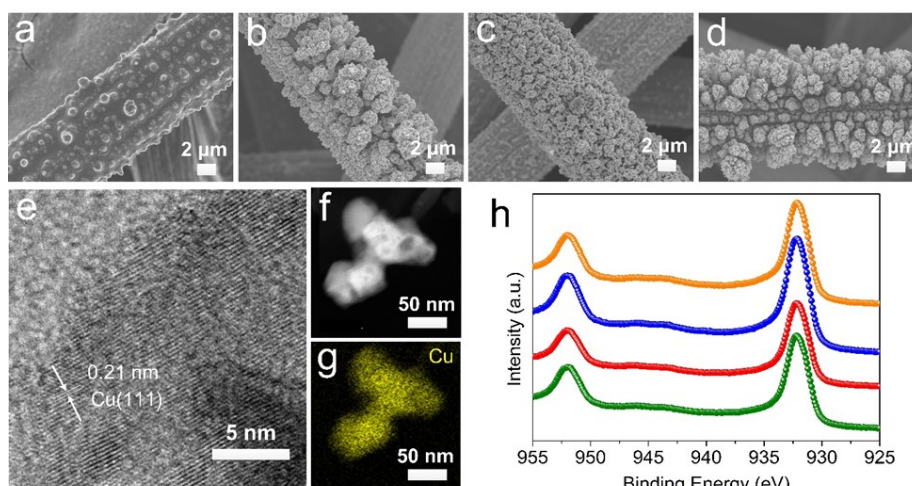
Fig. 7.1: Electron microscopy images of oxide-derived Cu electrodes with various roughness factors and corresponding X-ray photoelectron spectroscopy surface analyses.

Dr LIU Guanyu

There is a big research gap in the understanding of the mechanistic chemistry going on in an electrochemical cell to achieve appropriate Faradaic efficiencies. To better understand this, real-time analysis of the electrochemical CO_2 reduction products using PTRTOF MS is the best analytical technique that would provide the time dynamics of the eCO₂ products. There is a great potential to make use of the real time profiles to build the mechanistic models. These real-time measurements can further compliment the chemical kinetics measurements and computational modelling.

With the focus above mentioned, **Dr Divya NAGARAJ (Research Fellow, NUS)** is now capable of demonstrating the eCO₂ reduction products using PTR-TOF MS in real time. She was recently able to extend the application of PTR-TOF MS for degradation study of organic-inorganic hybrid perovskite solar cells. Although perovskite materials have produced significant energy conversion efficiencies, their commercial viability is still lacking because of their decreased long-term stability. Thus studying the products formed by decomposition of perovskite materials would help in understanding the reasons behind their short-term stability. PTR-TOF MS was used to identify the signature volatile products produced during the decomposition of organic hybrid perovskite materials under thermal stress. Signature volatile products like NH_3, CHN, $C_3H_3N_3$ and CH_4N_2 were identified and the kinetics of these products helps in proposing the mechanistic decomposition pathway.
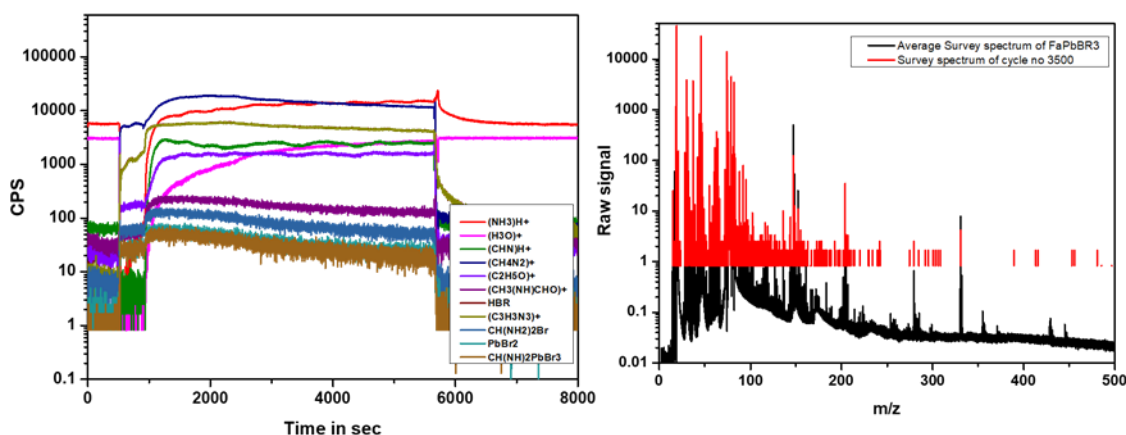

Fig. 7.2: Degradation study of FaPbBr₃ under thermal stress at 100 °C a) real time spectrum of FaPbBr3 showing the decomposition pattern of volatiles produced b) the corresponding survey spectrum of the FaPbBr₃.

Dr Divya NAGARAJ

Dr Hangjuan REN (Research Fellow, CARES) is working on electrochemical CO_2 reduction. This project intends to convert the greenhouse gas, CO_2, to constructive organic chemicals, especially ethylene. However, there are three main challenges: (i) CO_2 molecular is unreactive, (ii) driving the reaction towards any single product is difficult due to the complicated reaction pathways, (iii) stability of electrocatalysts is poor. In order to solve these problems, Dr Hangjuan Ren built up a flow-cell system and developed a new gas diffusion electrode. The present Cu-based electrode demonstrates a high current density of ethylene (198.7 mA/cm²) in 3.5 M KOH, at a low potential (only -0.67V *vs.* RHE). The Faradic efficiency of ethylene reaches 53% and the stability of this gas diffusion electrode is more than 3 hours. This electrode is synthesised by spray coating. Thus, it is easy to scale up this electrode and this gas diffusion electrode is promising for industrial application.
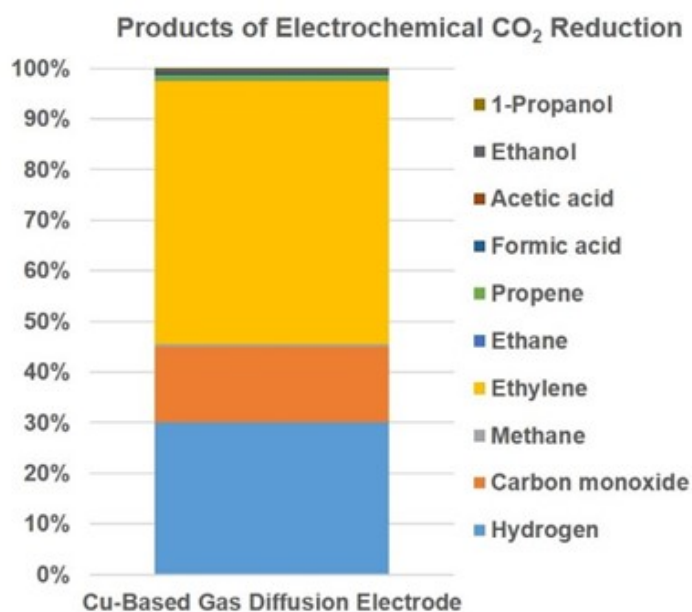
Fig. 7.3: Faradaic efficiency of reduction products.

Dr REN Hangjuan

SHEN JingJing (PhD student, NTU) and **Prof. Jason XU Zhichuan (PI, NTU)** employ the strategy of tetrahedral defects and oxygen vacancies in spinel oxide $LiCo_2O_4$ to realise the dual function of t_{2g} activation and oxygen transport in bulk materials to promote OER activity. Theoretical calculations in Figure 7.4 have shown that by inducing tetrahedron and oxygen vacancies, orbital crossings in the vicinity of the Fermi level were observed, which would facilitate electron charge transfer. Experimental studies show that by ther-
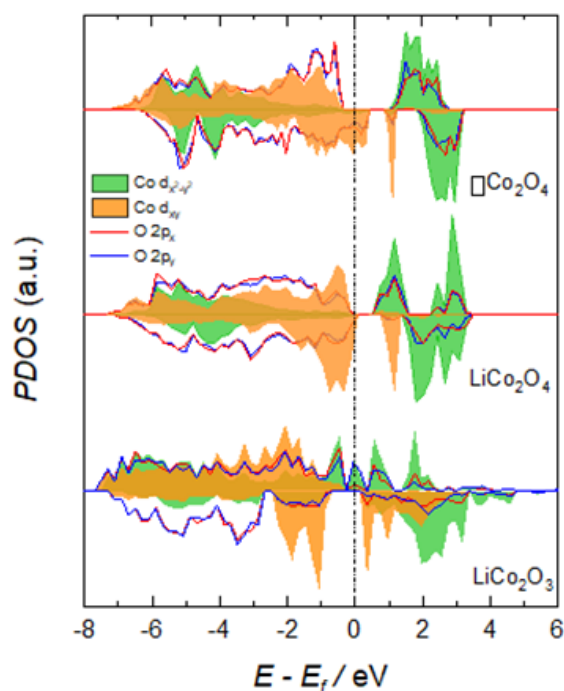
Fig. 7.4: PDOS of Li and O vacancies of LiCo2O4 of x-y plane.

Dr REN Hangjuan

mal decomposition, spinel oxides $LiCo_2O_4$ were synthesised at three temperatures, 300 °C, 400 °C and 500 °C. XRD patterns in Figure 7.5 have confirmed the spinel oxide structures of the synthesised materials. According to ICP-MS results, the atomic ratios of Li/Co of 0.42 (300 °C), 0.26 (400 °C) and 0.04 (500 °C) show that tetrahedron vacancies are induced with increasing heat treatment temperatures. TGA results as shown in Figure 7.6 estimate that 37.5% of oxygen is released as the temperature reaches 500 °C. In-situ XAS in Figure 7.7 show that more Co-O bonds form as annealing temperature is increased, indicating that more oxygen vacancies are present because more (oxy)hydroxides can be adsorbed onto the cobalt atom to fill up the oxygen vacancies.

Fig. 7.5: PXRD patterns of as-synthesised $LiCo_2O_4$ samples

Dr REN Hangjuan

Fig. 7.6: Thermogravimetric analysis of the $LiCo_2O_4$ sample.

Dr REN Hangjuan

Fig. 7.7: Fourier transforms (FT) of Co K-edge in-situ EXAFS of $LiCo_2O_4$ 300 °C-500 °C at 600 mV compared with ex-situ EXAFS of the respective samples.

Dr REN Hangjuan

Update on work package 2
Modelling and data informatics

Dr Quang Thang TRINH (Victor) (Senior Research Fellow, NTU), under the supervision of **Dr Matthew P. Sherburne (Co-PI, BEARS, University of California, Berkeley)**, performed Density Functional Theory (DFT) calculations to get the input data for the CO_2 electro-reductive micro-kinetic modelling on Cu-based catalyst. Based on transition state theory, the contribution of reaction temperature and applied p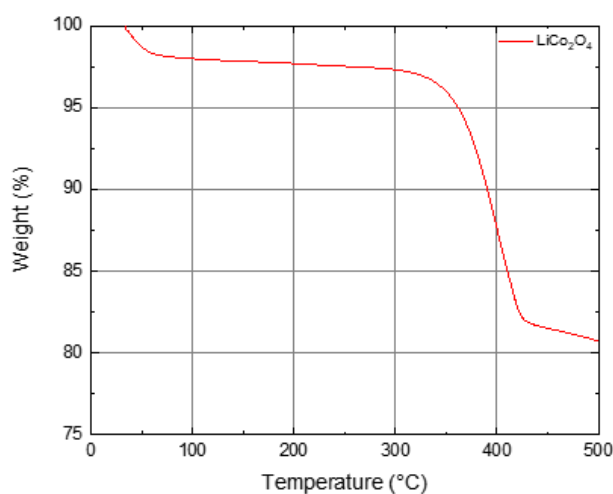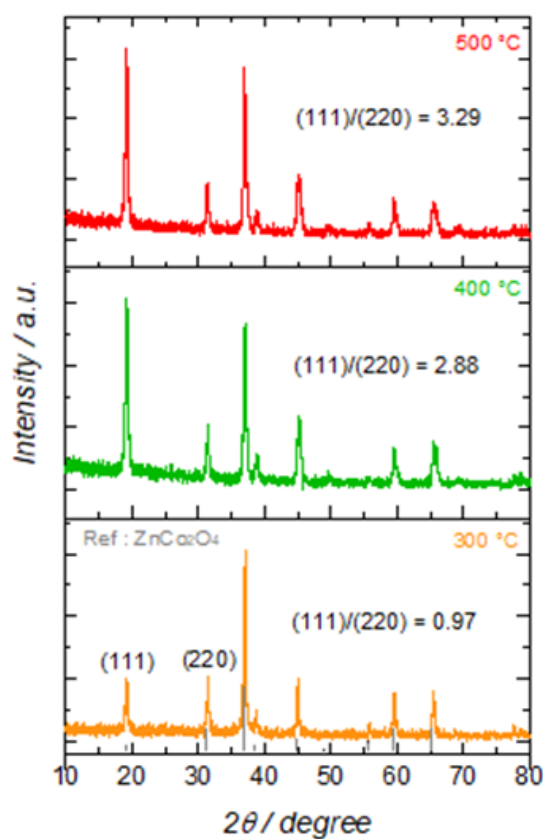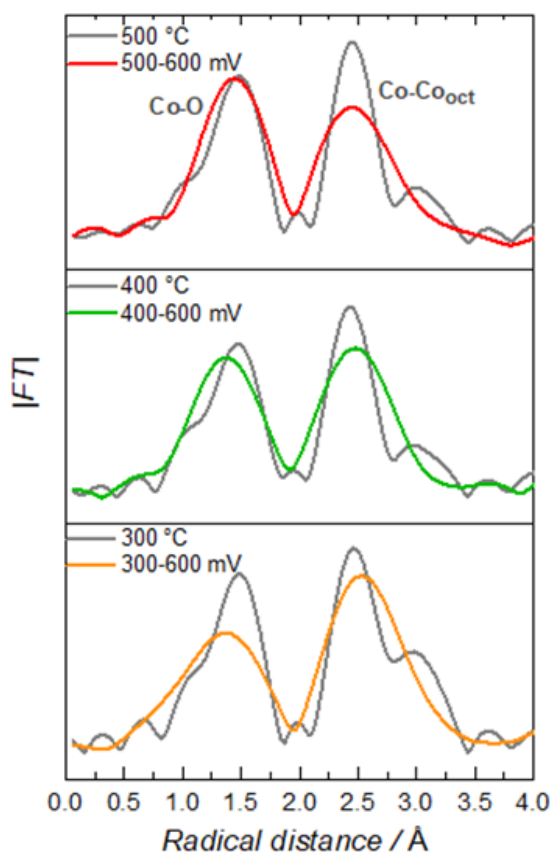otential to the pre-exponential factor and activation barriers for all elementary reaction steps were computed from first-principle calculations. The generated data then was used as input data for the micro-kinetic model, allowing evaluation of the catalyst performance and helping to scale the electrode/reactor design in Work Package 3.

Besides this, motivated from the importance and usefulness of the surface-enhanced Raman scattering (SERS) technique in studying and evaluating the structure of the Cu-based catalyst for the CO_2 reduction, Dr Quang Thang Trinh also conducted a DFT-based method for computing the SERS spectra for adsorbed molecules on the surface of transition metals. A chosen case study was the investigation of the interactions of chlorpyrifos (CPF), an intensively used pesticide, on a roughed silver nanoparticle surface. By combining both experimental and theoretical methods, the scheme of using DFT calculations in correctly predicting the SERS spectra for adsorbed species

was successfully developed, and insightful electronic interactions between the adsorbate and metal surface were revealed. The results from this study were accepted for publication in *The Journal of Physical Chemistry C*. This method would be very helpful when extended and applied to identify stable intermediates during CO_2 reduction on the Cu-based catalyst synthesised in eCO2EP.

Tuning the electronic properties of the catalyst is very important for achieving high selectivity and activity while maintaining good stability, in particular for the catalyst development research in eCO2EP. Furthermore, unsaturated (edge and corner) sites usually possess higher catalytic activity than normal active sites, however their presence on the catalyst surface is minimal. Dr Quang Thang Trinh also investigated how to control the structure of the catalyst in order to increase the exposure of those unsaturated active sites, together with evaluating the electronic properties of those sites to explain their nature of high activity. In the study in collaboration with Dr Paul LIU Wen (PI, NTU, C4T IRP1) and Dr John Mondal from India, Dr Quang Thang Trinh performed DFT calculations to reveal two possible roles of TPT-POP in contributing to the highly selective hydrogenation of C=C bond on the Pd-Fe_3O_4 catalyst support on hydroxyl enriched Porous-Organic-Polymers (called TPT). Firstly, TPT acted as a structural template for generating

highly concentrated Pd step site and other low coordinated sites, which possess high activity towards C=C bond hydrogenation. Secondly, the charge transfer from TPT to the Pd clusters increased the negative charge density on the Pd sites, consequently enhancing their C=C hydrogenation activity. The results from this study provided new inspirations for designing easily realisable, low-cost and high-performance catalysts for sustainable chemistry via effective surface/interface engineering. This study was accepted for publication in the *ChemCatChem* journal.

Finally, Dr Quang Thang Trinh also actively contributed in writing review papers and book chapters on the current status and future perspectives for biomass utilisation and the development of photocatalysts, providing alternative pathways to reduce the CO_2 footprints. The review paper was published in the *Journal of Cleaner Production* and the book chapters were included in works published by Nature Springer.
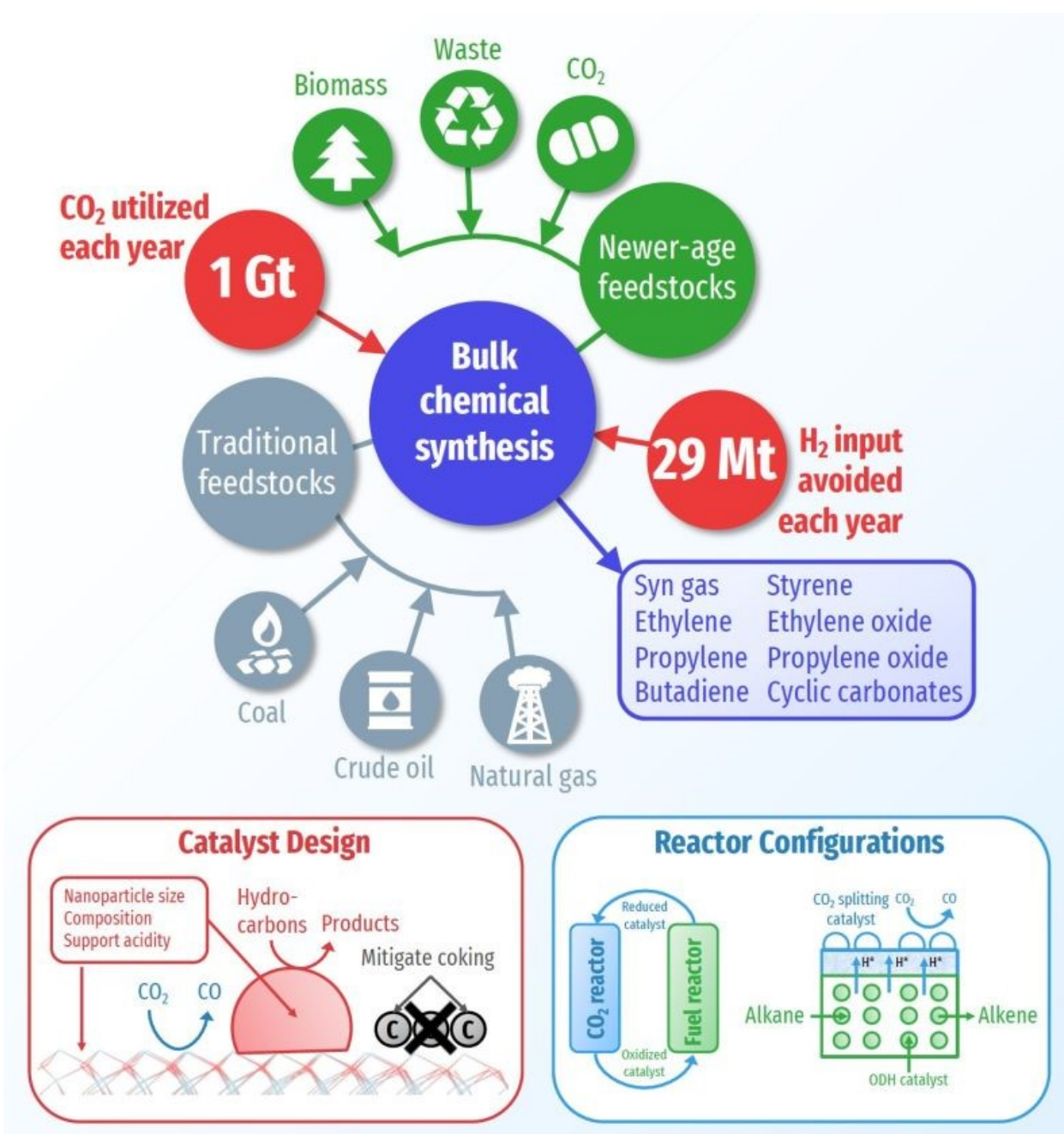
Update on work package 3
Chemical factory on a table

Dr Magda BARECKA (Research Fellow, CARES) is mainly involved in the whole plant design/integration and process optimisation for the table top factory converting carbon dioxide to ethylene. Over the last few months, she has been focusing on development of energy efficient approaches for liquid products separation and has designed, commissioned and troubleshot an experimental set-up for vacuum membrane distillation of PTFE membrane (Figure 7.8). First results have been obtained indicating that this separation is suitable for separation of ethanol from a highly alkaline solution and has the potential to be implemented into the plant design.

Dr Magda Barecka also continues to support the development of the flowsheet for the overall mini-plant delivered within the eCO2EP project. Furthermore, she has been continuing the work on industrial implementation of carbon dioxide to ethylene electroconversion technology. She has determined several new niches for the technology application, which resulted in submission of a new patent for a 'Process for recycling of waste carbon dioxide in ethylene-based manufacturing plants'. This application extends the scope of the previous patent application. Discussions about the commercialisation of this technology are ongoing with, for example, BASF and Magda is cur-

Fig. 7.8: Overview of the experimental set-up for vacuum membrane distillation, suitable to separate CO_2 conversion liquid products from highly alkaline electrolyte solution.

Dr Magda Barecka

rently applying for supplementary funding to further de-risk this technology and make it more attractive for the end user.

Dr Magda Barecka is also developing CO_2 recycling concepts for other products than ethylene. These concepts can have a remarkable potential to reduce CO_2 emissions from the chemical industry.

Dr Alexandr KHUDOROZHKOV (Research Fellow, CARES) has collected and processed chemisorption data of some samples. It was shown by pulse chemisorption analysis that adsorption capacity of the 4Å molecular sieves is 0.21 cm³/g for carbon dioxide, whereas it was measured as 0.18 cm³/g for ethylene. As a result, low surface area and close adsorption capacity of target molecules should lead non-modified 4Å molecular sieves to be considered as an unsuitable material for the storage or separation of ethylene and carbon dioxide. However, modification

of the zeolite structure and its affinity to ethylene via ion exchange with Cu, Ni and Ag could lead to the gradual increase of its performance in ethylene adsorption and separation. Further pulse chemisorption and breakthrough experiments for the abovementioned materials together with earlier synthesised MOFs should help us to select the most efficient adsorbent.

Chabazite type zeolite (CHA) was synthesised as a promising material for the liquid-liquid separation of ethanol and water in highly basic media. To test the stability of the chabazite, a fresh sample had been stored in 7M KOH solution for 10 days (aged sample). It is planned to compare the XRD and BET surface area data of fresh and aged samples to approve the stability of the zeolite. Time resolved absorption of ethanol from solutions with different C2H5OH:H2O ratios will be used to test the CHA liquid separation efficiency.
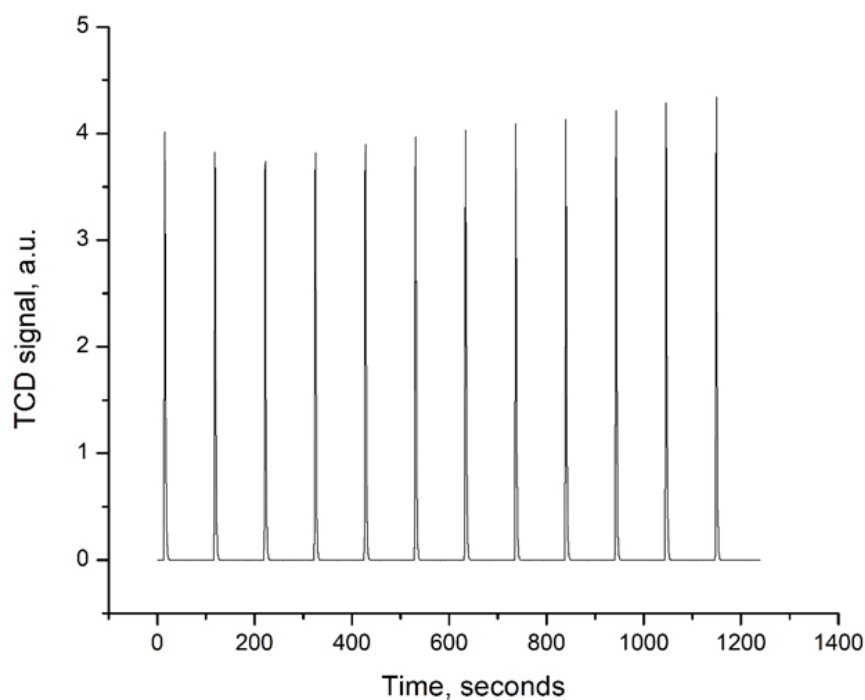

Fig. 7.9: Pulse chemisorption data of the adsorption of C_2H_4 on 4Å molecular sieves.

Dr Alexandr KHUDOROZHKOV

Shishir JAIRAM (Research Engineer, CARES) has been working on large scale design and development of a pilot plant for carbon capture. He has currently worked on development of the process flow diagrams, design of the reactor and the engineering. His initial task was to develop a suitable flow diagram to help in the design of the pilot plant, with the process flow diagrams. Initially, the main goal was to completely design the reactor and thus assist improve the complete reactor facility. Numerous software programs like Autodesk Inventor, SolidWorks and Siemens NX software were used for the extraction of the flow field of the gas channel. Shishir Jairam finalised the design after complete optimisation of the design and the engineering works on the 3D printed reactors. The COMSOL software was used to extract the flow channels and help to simulate them. The complete reactor assembly is as shown below.

The plant assembly process mainly included the assembly and calibration of the pump, calibration of the mass flow controllers and calibration of the power source. With the help of video calls, Shishir Jairam has calibrated the system. Mechanical assembly has been completely finished, the major wiring and software installation is underway. He is also ensuring that all the safety standards are being adhered and all the risk assessments have been completed. The assembly of the pilot plant also included fabricating the frames; this is being done inhouse and currently the fabrication is underway. A 3D printer was also used to help with fabrication of tiny components such as washers, screws and tubing.

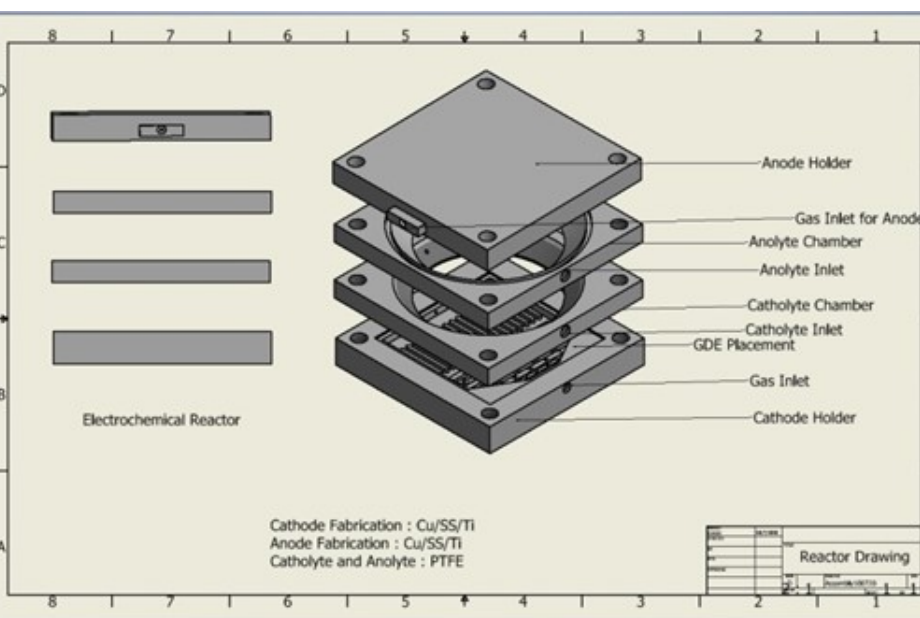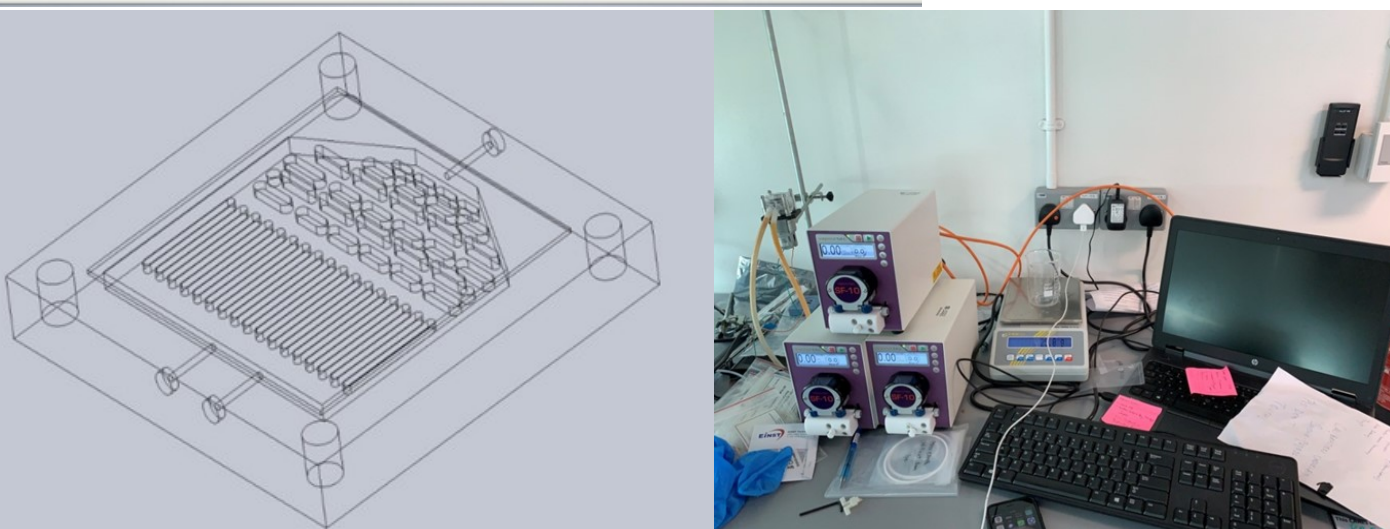Shishir Jairam has started working on automation of the entire plant and thus the next step is underway.

Fig. 7.10: Reactor design as well as automation and calibration of the pumps.

Shishir JAIRAM

Scientific output

The following are the CREATE-acknowledged publications generated by eCO₂EP during the reporting period, excluding those already featured in the Scientific Highlights section on page 17.

Conversion of lignocellulosic biomass to fuels and value-added chemicals using emerging technologies and state-of-the-art density functional theory simulations approach

P. N. Amaniampong, N. Y. Asiedu, E. Fletcher, D. Dodoo-Arhin, O. J. Olatunji and Q. T. Trinh in *Valorization of Biomass to Value-Added Commodities. Green Energy and Technology Book Series (GREEN). Cham: Springer International Publishing*

Abstract: In recent years, the drive toward a sustainable economy has challenged the scientific community to pursue ambitious investigations to convert sustainable feedstocks such as lignocellulose into useful products. These products include biofuels, commodity chemicals, and new bio-based materials including bioplastics, which offer a potential substitution to the dwindling nonrenewable fossil resources. A plethora of lignocellulosic biomass processing technologies have been attempted and effectively documented in literature, which include, but not limited to, biochemical, liquid acid, thermochemical, and catalytic (homogeneous and heterogeneous catalysis) transformation processes. This chapter reviews the state-of-the-art research and development of these process technologies. We further highlight the advantages and disadvantages, potential for future applications, challenges related to these technologies, and opportunities to maximize economic and environmental benefits, while minimizing waste and pollution. Special emphasis is placed and discussed on the production of biofuels and commodity chemicals from these process technologies. Besides, the application of molecular modeling in integration with experiments is highlighted in this chapter as a new paradigm for mechanism study and thus could open up new avenues to design and develop catalysts for a plethora of biomass reactions that require high activity and selectivity.

SERS spectra of the pesticide Chlorpyrifos adsorbed on silver nanosurface: The Ag20 cluster model

Thi Chinh Ngo, Quang Thang Trinh, Nguyen Thi Thai An, Nguyen Ngoc Tri, Nguyen Tien Trung, Dinh Hieu Truong, Bui The Huy, Minh Tho Nguyen and Duy Quang Dao, *The Journal of Physical Chemistry C*

Abstract: In recent years, the drive toward a sustainable economy has challenged the scientific community to pursue ambitious investigations to convert sustainable feedstocks such as lignocellulose into useful products. These products include biofuels, commodity chemicals, and new bio-based materials including bioplastics, which offer a potential substitution to the dwindling nonrenewable fossil resources. A plethora of lignocellulosic biomass processing technologies have been attempted and effectively documented in literature, which include, but not limited to, biochemical, liquid acid, thermochemical, and catalytic (homogeneous and heterogeneous catalysis) transformation processes. This chapter reviews the state-of-the-art research and development of these process technologies. We further highlight the advantages and disadvantages, potential for future applications, challenges related to these technologies, and opportunities to maximize economic and environmental benefits, while minimizing waste and pollution. Special emphasis is placed and discussed on the production of biofuels and commodity chemicals from these process technologies. Besides, the application of molecular modeling in integration with experiments is highlighted in this chapter as a new paradigm for mechanism study and thus could open up new avenues to design and develop catalysts for a plethora of biomass reactions that require high activity and selectivity.
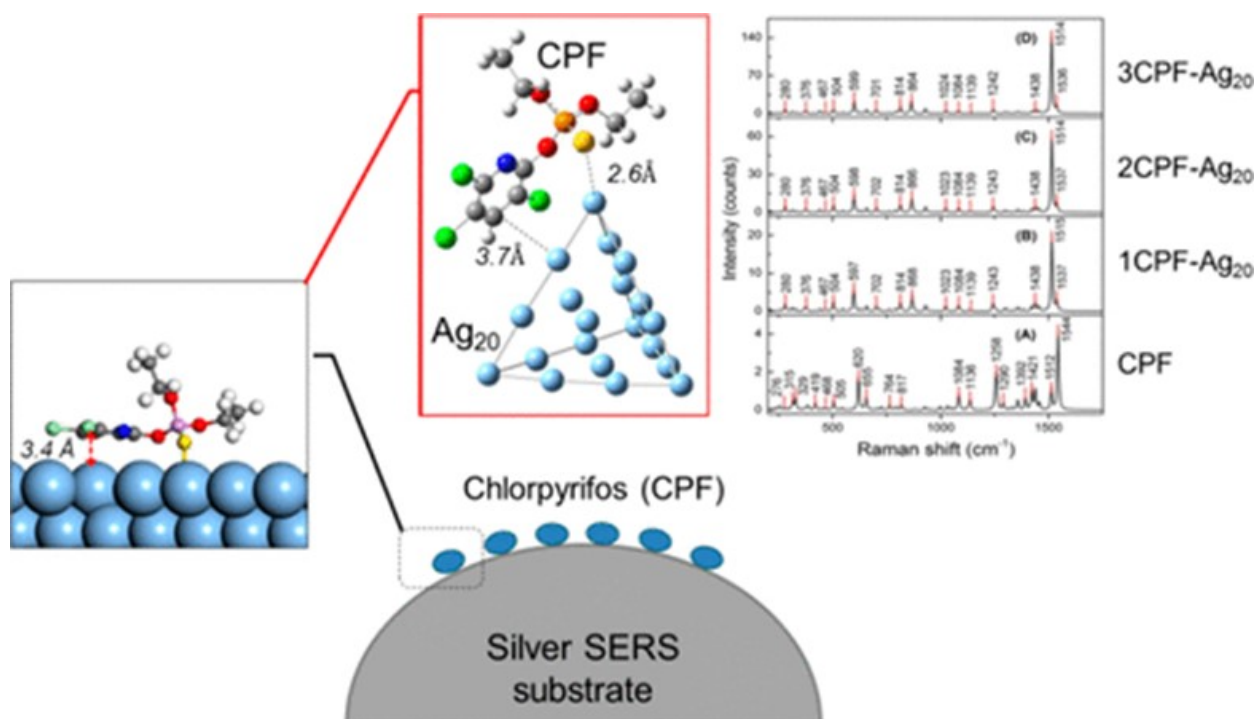
Upgrading of bio-oil from biomass pyrolysis: current status and future development

Quang Thang Trinh, Arghya Banerjee, Khursheed B. Ansari, Duy Quang Dao, Asmaa Drif, Nguyen Thanh Binh, Dang Thanh Tung, et al. *In Biorefinery of Alternative Resources: Targeting Green Fuels and Platform Chemicals*

Abstract: For the sustainable production of fuel, biomass pyrolysis processes have appeared as a promising alternative for the efficient utilization of biomass. The liquid product obtained from biomass pyrolysis, i.e., bio-oil has a very complex composition including large proportion of organic oxygenated hydrocarbon compounds and appreciable amount of water. The high oxygen content of the bio-oil creates many major drawbacks that hinder its vast application. The quality of bio-oil is not applicable for direct transportation purposes, and its upgrading is mandatory before it can be used practically in power engines. The abovementioned drawbacks can be overcome by the catalytic hydrodeoxygenation of bio-oil, in which the functional groups containing oxygen are removed and replaced by hydrogen atoms. For this purpose of selectively activating and breaking the C–O bonds while trying to maintain the C–C bonds intact, processing knowledge base of petroleum industry may not be utilized for hydrodeoxygenation of bio-oil. Therefore, novel catalysts, solvents, and processes need to be developed. This chapter reviews the state-of-the-art results obtained from the research and development of these technologies. The pros and cons, potential of future applications, challenges related to these technologies, and opportunities to maximize economic and environmental benefits while minimizing pollution are highlighted. Besides, the application of molecular modeling in the integration with experiment is highlighted in this chapter as a new paradigm for mechanistic studies, which could open new avenues to design and develop catalysts for a plethora of bio-oil upg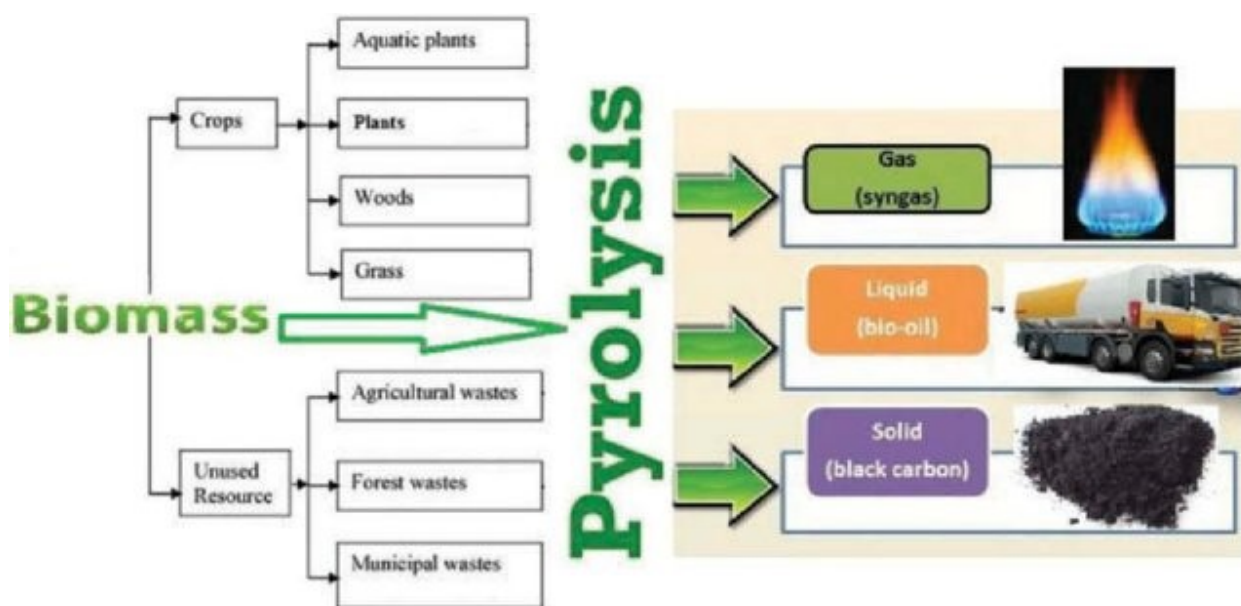rading processes that require high activity and selectivity. Finally, the breakthrough applications of novel sonochemical technique in biomass treatment and conversion are introduced in this chapter.

Capability of *Aganonerion Polymorphum* leaf-water extract in protecting hydrochloric acid induced steel corrosion

Pham Van Hien, Nguyen Si Hoai Vu, Lai Xuan Bach, Ngoc Quyen Tran, Vinh Ai Dao, Quang Thang Trinh and Nguyen Dang Nam, *New Journal of Chemistry*

Abstract: The requirements for an alternative to toxic localized corrosion inhibitors have always been high-performance with localized corrosion inhibition, availability, ease of manufacturing, cost-effectiveness and ecological safety. Due to its reputation in South East Asian countries as a vegetable of low-cost and environmental friendliness, Aganonerion polymorphum, or rather its leaf extract, can be a source of environmentally friendly and high-performing inhibitors. The effect of water extract of Aganonerion polymorphum leaf (APLWE) on carbon steel in 0.1 M naturally-aerated HCl solution was studied as a potential corrosion inhibitor using electrochemical techniques and surface analyses. The outcome demonstrated the mixed inhibition behavior of APLWE on the steel surface in holding back the electrochemical corrosion reactions by the establishment of a highly resistive layer, resulting in a reduction of the corrosion penetration rate. Surface appraisals indicated the existence of an adsorbed film as a complex between metal ions and an organic film of APLWE components, thereby preventing a case of corrosive degradation on the steel. The details of theoretical methods are in close agreement with experimental results, which confirmed the role of APLWE as an inhibitor through adsorption activities, providing corrosion resistance for steel in a hydrochloric environment.
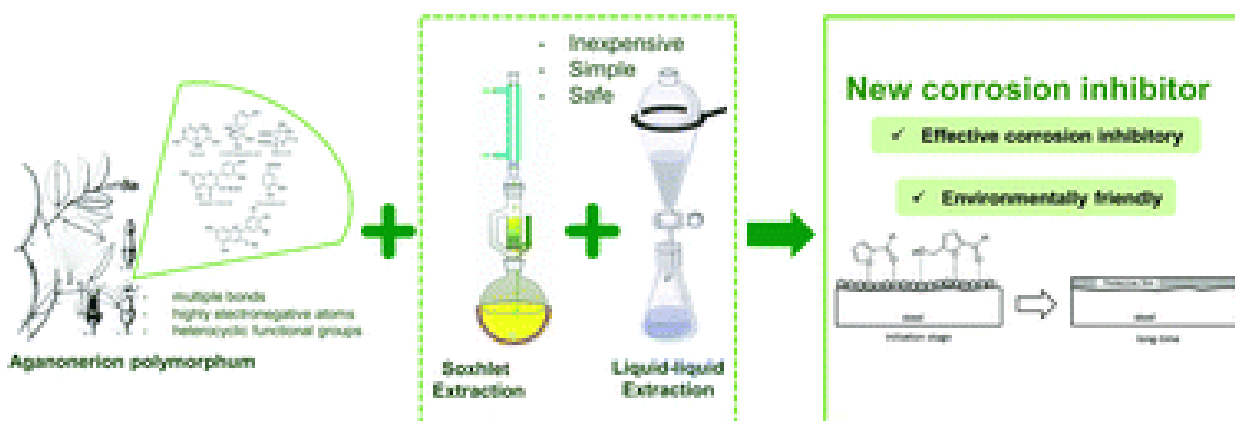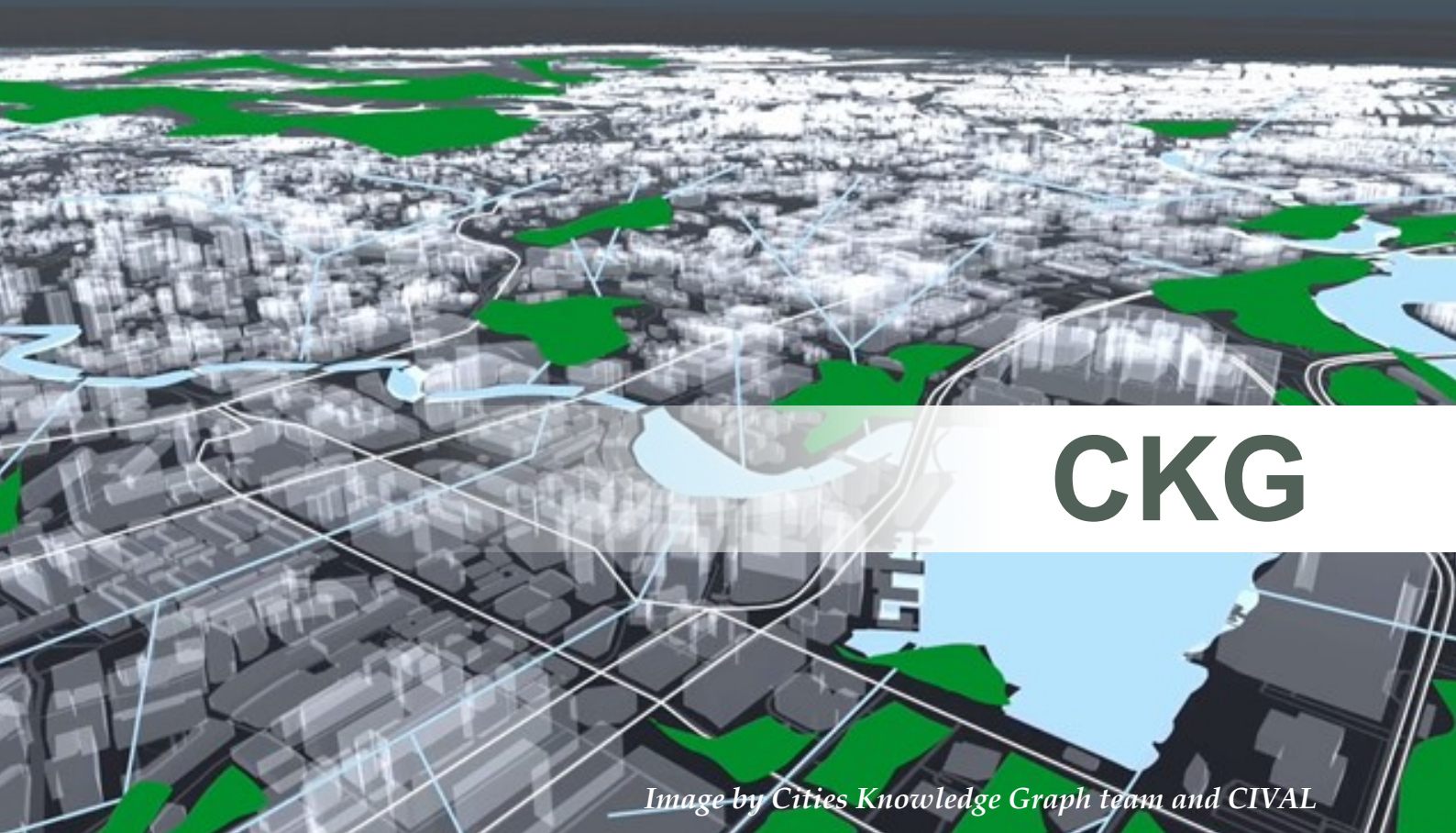
Image by Cities Knowledge Graph team and CIVAL

CKG

CITIES KNOWLEDGE GRAPH

Cities Knowledge Graph (CKG) aims to transform master-planning related data, information and knowledge into a semantic and extensible platform – a knowledge graph. The proposed CKG would be similar to a knowledge management system for urban planning, integrating information from various sources and domains, evaluating planning proposals against visions and targets set for future urban development, and supporting policy makers and planners by mapping interesting planning directions. It further ties together existing 3D geo-databases, such as URA Space, as well as novel analysis, simulation and visualisation tools developed by CARES and SEC, creating an unprecedented knowledge graph for master-planning.

CKG Principal Investigators:

Professor Markus KRAFT
University of Cambridge

Professor Stephen Cairns
ETH Zürich

OVERVIEW

Cities-planning Knowledge Graph (CKG) is an Intra-CREATE collaborative project in the urban systems thematic area. The project brings together expertise from Cambridge CARES, the host institution of the project, and SEC (the Singapore-ETH Centre, established by ETH Zürich—the Swiss Federal Institute of Technology Zürich). The team is led by Principal Investigators from University of Cambridge (Prof. Markus Kraft) and ETH Zürich (Prof. Stephen Cairns). Dr Aurel von Richthofen (Senior Researcher, SEC) and Dr Pieter Herthogs (Senior Researcher, SEC) are Co-Investigators of the project.

The project is in the process of recruiting researchers. Over the past six months, we have conducted a systematic literature review to explore the intersection of two core concepts that will be defined to enable interdisciplinary research: "City Planning" and core levels of the Semantic Web. We have also been working on developing a master-planning ontology for Singapore based on the URA Space. An intermediate outcome of this work is a Unified Modelling Language (UML) class diagram depicting the data, including boundaries of different levels of planning areas, roads, plots, demographics, urban design guidelines for specific areas, etc.

Furthermore, we have verified a subset of OntoCityGML ontology required for incorporating CityGML data into the knowledge graph. This subset of OntoCityGML ontology has been checked for consistency and new ontology unit test cases for over 50 selected concepts have been incorporated. In addition, after conducting preliminary assessment of various available storage systems, it was concluded that the Blazegraph, an open-source ultra high-performance graph database, is a promising candidate to be used as a storage system for this project. Consequently, we have extended an existing importer-exporter tool to support connection to the Blazegraph in order to handle the huge volumes of geographical data required by the project.

Professor Markus Kraft, PI
University of Cambridge

Professor Stephen Cairns, PI
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Update on work package 1
Developing master-planning ontologies

This work package aims at developing the master-planning ontologies for the Singapore Master Plan. We will approach this by reviewing and assessing relevant existing master-planning data, software, practice and ontologies.

Dr Aurel von RICHTHOFEN (Senior Researcher, SEC) and **Dr Pieter HERTHOGS (Senior Researcher, SEC)** have conducted a systematic literature review to explore the intersection of two core concepts that will be defined to enable interdisciplinary research: "City Planning" and core levels of the Semantic Web. Both terms have a legacy of accumulated meanings that are difficult to penetrate for outsiders. City Planning, as a complex practice relating various knowledge domains, actors, spatial and temporal scales, will be categorised in terms of Representation, Creation,

Evaluation, and Information Processing (Figure 8.1). To this end, Dr Aurel von Richthofen and Dr Pieter Herthogs have conducted a systematic literature search to explore the size, distribution, and gaps in the literature. To underscore the interdisciplinary characteristics and the societal relevance of the topic, they have traced the historical origins of the ideas of Semantic City Planning. They have also further looked into the state-of-the-art of Semantic City Planning Support and examined tools exploring semantically linked data for urban knowledge production. Dr Aurel von Richthofen and Dr Pieter Herthogs are in the process of preparing an article that reviews and structures existing research related to Semantic City Planning Support.

Fig. 8.1: This diagram represents the four core actions of City Planning processes:

- *Representation (the act of representing particular urban environments)*

- *Creation (the act of designing or envisioning materialisations or characteristics for a particular future urban environment)*

- *Evaluation (the act of evaluating urban environments)*

- *Information Processing (the act of using, managing, creating, and synthesising data, information, and knowledge)*

These actions do not need to occur in a particular order, and each of these actions happens at several times and scales, following different iterations.

Each of these four core actions supports the main action of a City Planning process: Decision-making (the act of making decisions).
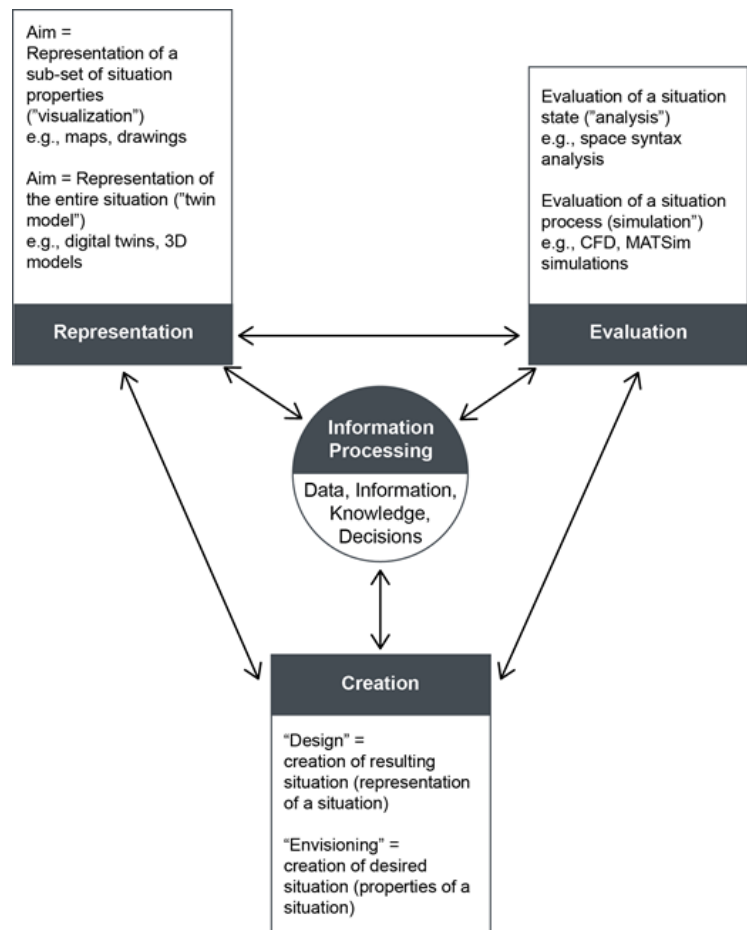
Dr Zhongming SHI (Postdoctoral Researcher, SEC) and **Dr Pieter HERTHOGS** have been working on developing a master-planning ontology for Singapore based on the URA Space. The URA Space provides a set of structured data on the Singapore Master Plan supplied by the Singapore's Urban Redevelopment Authority. Dr Zhongming Shi and Dr Pieter Herthogs have developed a Unified Modelling Language (UML) class diagram depicting the data, including boundaries of different levels of planning areas, roads, plots, demographics, urban design guidelines for specific areas, etc. A snippet of the UML class diagram is shown in Figure 8.2. The development of a master-planning ontology based on this set of data intends to lay the foundation for the extensible semantic platform for urban planning proposed by the CKG and can be related to ei-

ther one of the above-mentioned four planning actions.

Dr Zhongming Shi has also been working on integrating the toolbox City Energy Analyst (CEA) into the CKG. CEA is an open-source toolbox for urban building energy modelling, developed at the ETH for the past nine years, which is able to simulate building energy consumption, energy supply system operation, and perform design optimisation of energy supply systems in a district. Dr Zhongming Shi has developed a UML activity diagram depicting the workflow of the CEA, along with the inputs and outputs for each CEA function. A snippet of the UML activity diagram is shown in Figure 8.3. Ontologies will be developed to semantically describe the classes and concepts utilised in CEA.
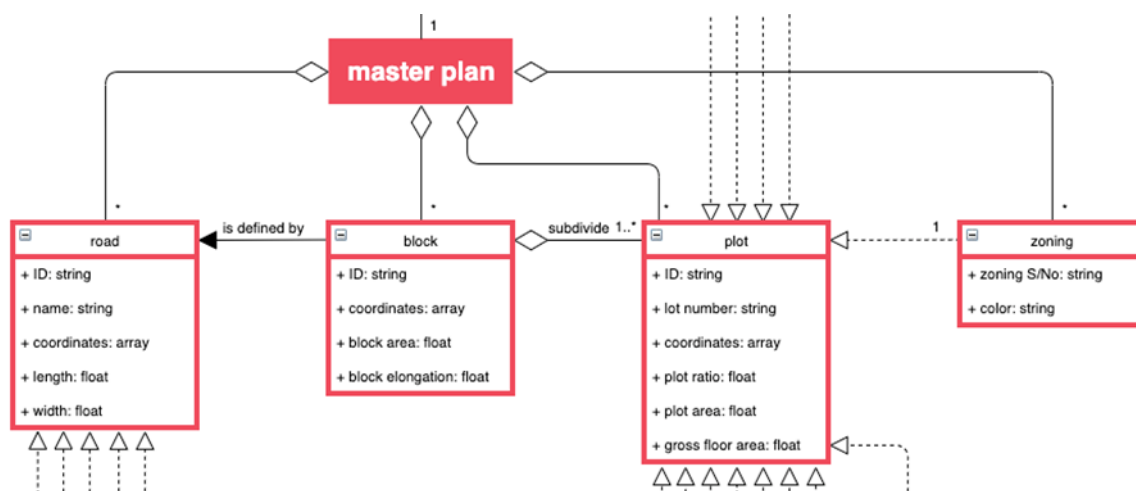
Fig. 8.2: Snippet of a Unified Modelling Language (UML) class diagram depicting the classes and concepts represented on the URA Space, the web platform of Singapore's Urban Redevelopment Authority for publicly available planning-related information (https://www.ura.gov.sg/maps/). These classes will form the basis for creating an ontology for the URA Space, and master-planning in Singapore.
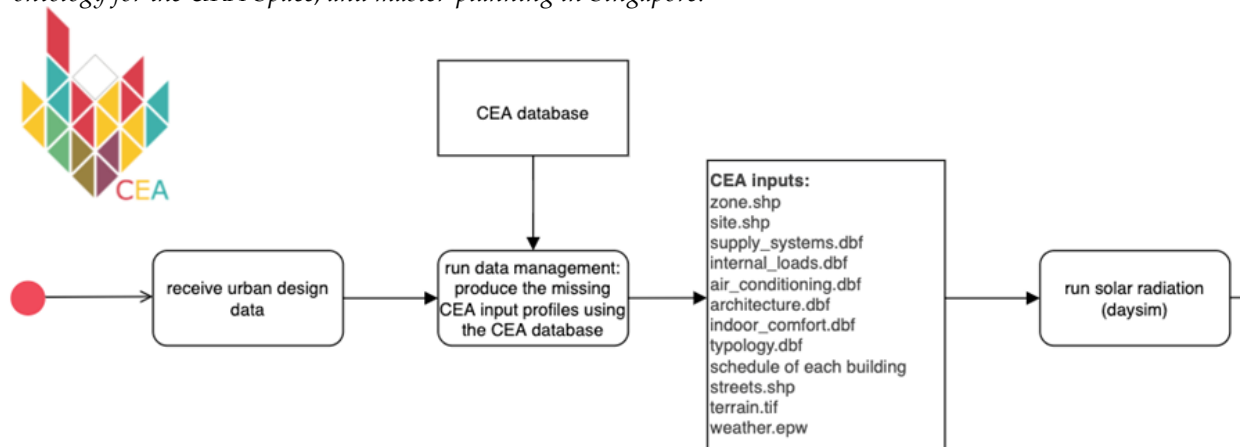
Fig. 8.3: Snippet of a Unified Modelling Language (UML) activity diagram depicting the workflow of the City Energy Analyst (CEA), which is to be integrated in the CKG.

Update on work package 2

Developing the knowledge graph's architecture

This work package aims at developing the knowledge graph's architecture in order to make use of the full potential of Semantic Web technologies. We will approach this by developing 1) agent ontology to describe the agents' functionalities and characteristics to enable agent discovery and composition; 2) semantic agent composition framework to facilitate automatic agent discovery and composition, to dynamically generate cross-domain applications and to provide information for decision-making; 3) "Parallel world" functionalities to facilitate design space exploration and 4) decentralised architecture to facilitate the integration of data repositories.

Arkadiusz CHADZYNSKI (Senior Research Fellow, CARES), Dr Pieter HERTHOGS (Senior Researcher, SEC) and Dr Nenad B. KRDZAVAC (Senior Software Developer, CARES) have been working on verifying a subset of OntoCityGML ontology required for incorporating CityGML data for Berlin into the knowledge graph. This subset of OntoCityGML ontology has been checked for consistency and new ontology unit test cases for over 50 selected concepts have been incorporated. It was discovered that, due to the expressivity of the OntoCityGML ontology, ontology-based data access (OBDA) technologies are not suitable for this purpose. After conduct-

Fig. 8.4: Extension of TU Munich 3D database importer-exporter tool for connection to the Blazegraph.

Arkadiusz CHADZYNSKI

ing preliminary assessment of various available storage systems, Arkadiusz Chadzynski concluded that the Blazegraph is a promising candidate to be used as a storage system for this project. Blazegraph is an open-source ultra high-performance graph database which is currently used by WikiData.

Arkadiusz Chadzynski is also involved in partially extending an existing importer-exporter tool, developed at TU Munich for the past nine years, in order to handle the huge volumes of geographical data required by the project. The TU Munich 3D database importer-exporter tool is an open-source code, originally designed to work only with relational databases. As the tool's design is based on Java Database Connectivity (JDBC) Application Programming Interfaces (APIs), it was possible to reuse substantial portions of the tool and extend it to suppor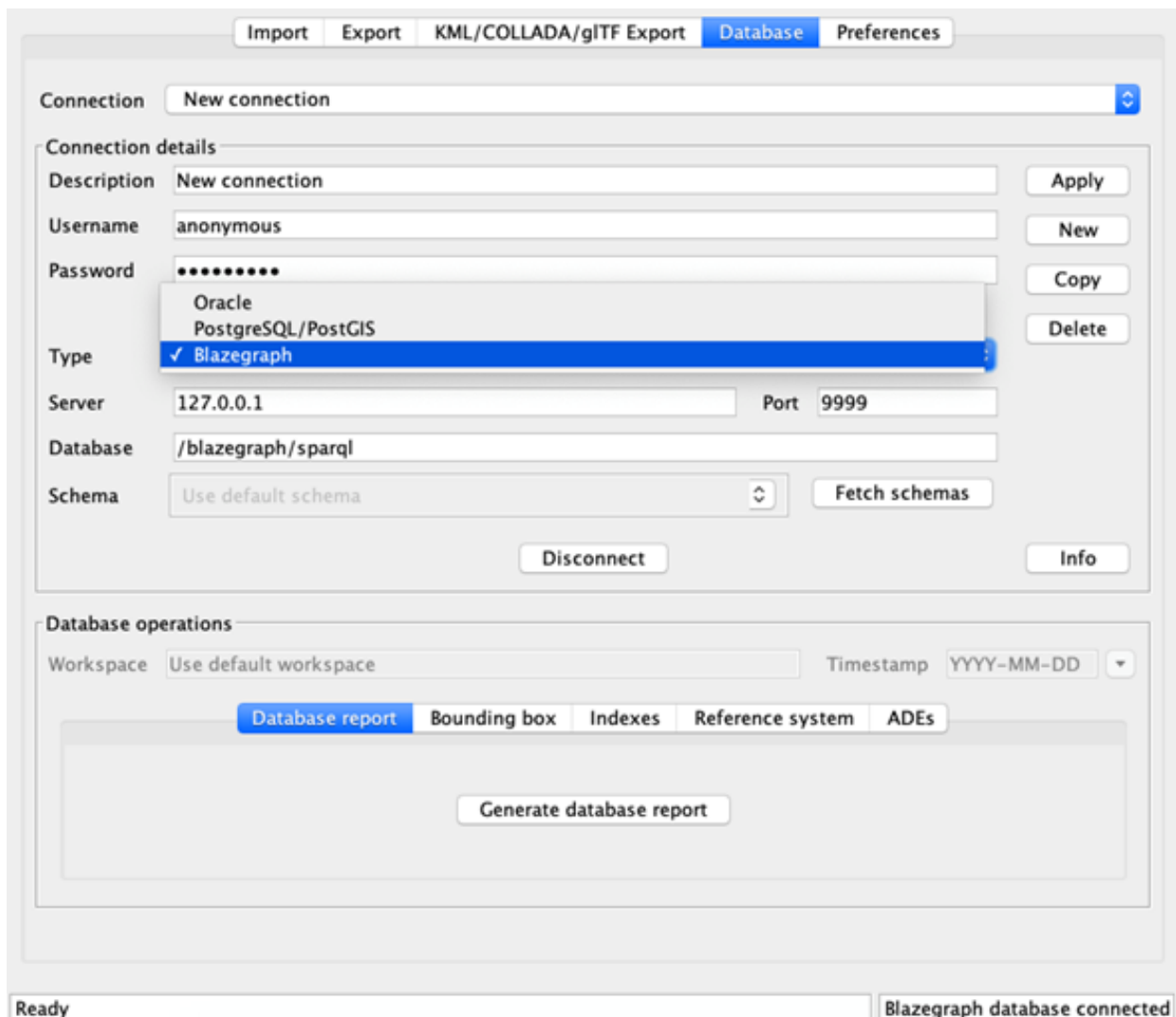t connection to the Blazegraph. The extension was implemented based on existing W3C standards by using Jena SPARQL over HTTP protocol JDBC driver. Figure 8.4 illustrates this extension with established connection.

Update on work package 3
Developing agents to operate software and integrate data

This work package aims at developing agents to operate software and integrate data in order to populate the knowledge graph. We will approach this by developing agents for data pre-processing, packaging existing and new planning libraries as agents and incorporate them into CKG using ontologies and developing reasoning and inference capabilities to facilitate design space exploration and scenario analysis.

This work package has not yet started in its entirety as the project is in the process of recruiting post-doctoral researchers for this work package.

Update on work package 4
Developing interfaces and planning libraries for the CKG

This work package aims at developing interfaces and planning libraries in order to allow stakeholders to interact easily with an interface to e.g. receive information about a planning area, ask "smart queries", or input a range of planning scenarios they would like the CKG to explore and analyse. We will approach this by developing planning libraries (agents) that can perform certain planning actions (master-planning tasks) based on user input.

This work package has not yet started in its entirety as the project will welcome its first software developer (SEC) for this work package in October.

Update on work package 5
Developing design informatics functions

This work package aims at developing models and algorithms to analyse planning capacities and potentials, and visualisation modes for the models to inform stakeholders. We will approach this by developing specific models or algorithms, integrating existing metrics where possible, and developing several metrics to inform the outcomes of particular planning actions in order to compare or evaluate different planning proposals or scenarios.

This work package has not yet started in its entirety as the work is planned to start in the second half of the first year.

Update on work package 6

Demonstrators: horizontal and vertical use cases

This work package aims at developing two use cases: one horizontal and one vertical use case, in order to demonstrate the potential applications and extensibility of the CKG approach. Each use case applies similar planning actions, but at different levels of granularity, demonstrating the scalability of the CKG.

This work package has started in the form of planning use cases for developments in work packages 1 and 2.
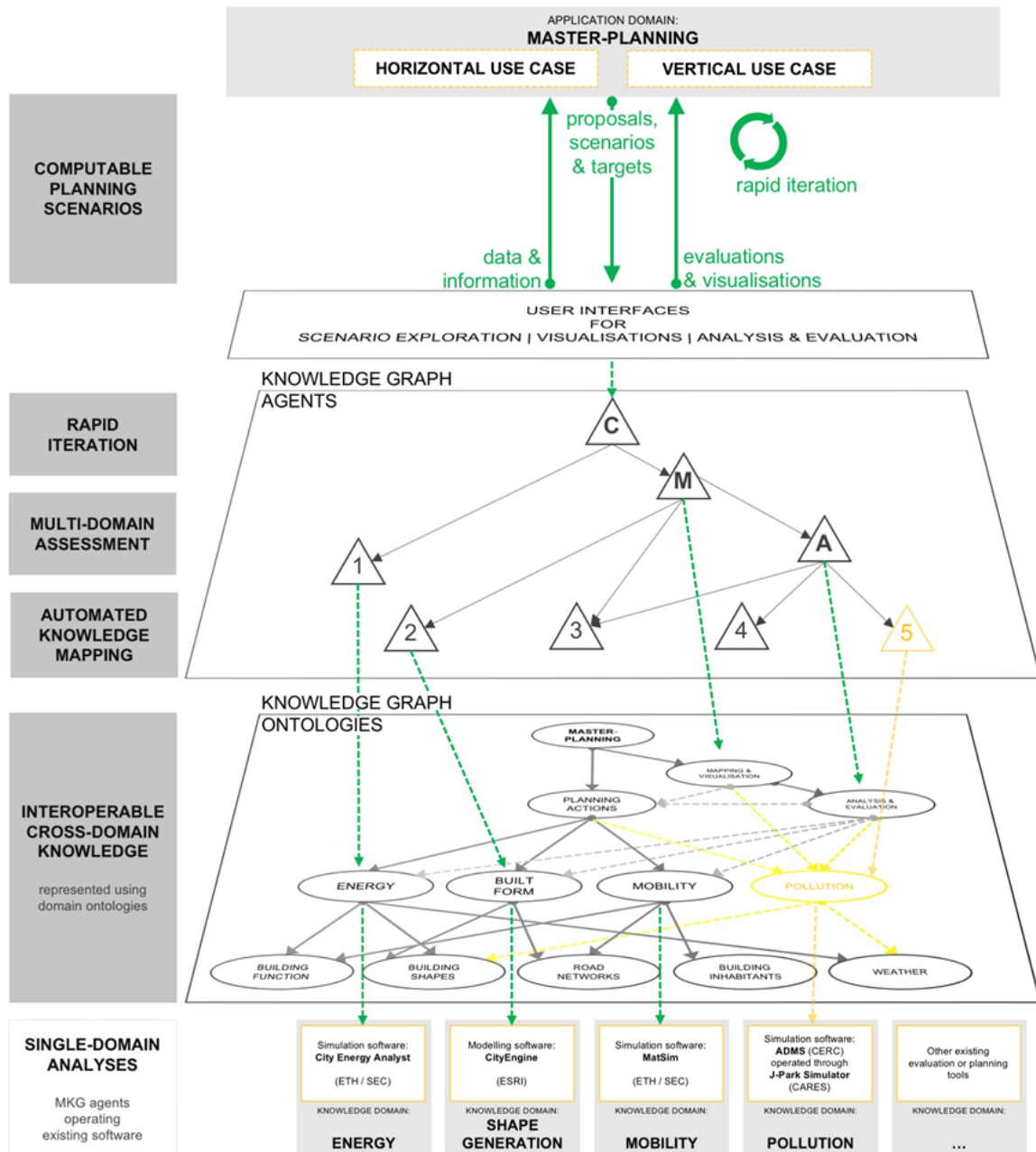
Fig. 8.5: This diagram illustrates how CKG would bridge the gap between conventional master-planning actions (as represented by our horizontal and vertical use cases) and individual knowledge domains within urban science (as represented by existing software developed and used by SEC and CARES). Benefits of the CKG are listed on the left. Existing applications are highlighted in orange.
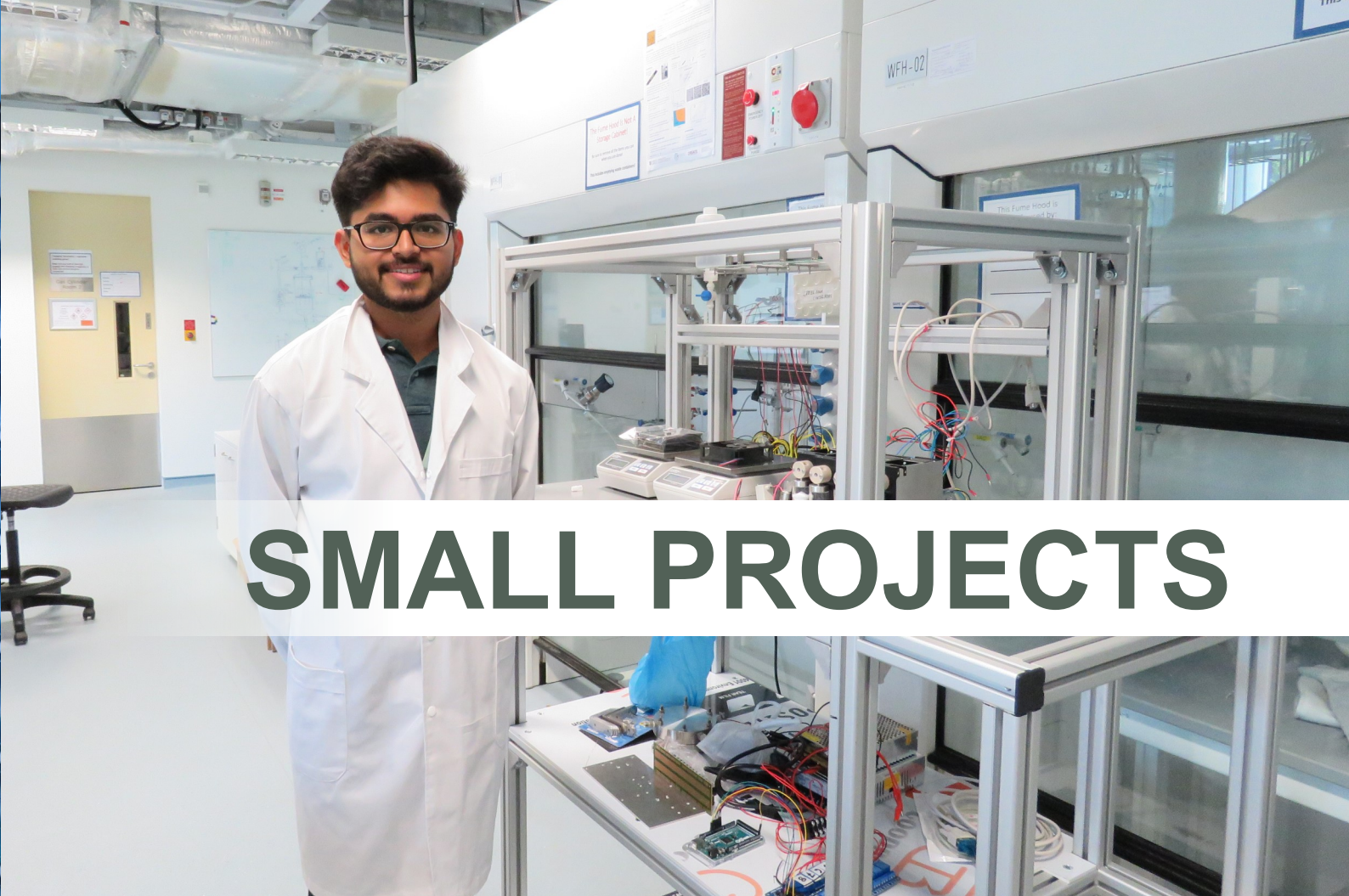
SMALL PROJECTS

OTHER CARES-FUNDED PROJECTS

In addition to C4T and eCO$_2$EP, CARES hosts a number of other projects. These give our researchers an opportunity to explore new areas, develop technologies for commercialisation or build relationships with new industry partners or public sector collaborators. The smaller projects are also often a good opportunity for interns (such as Aman SINGHAL, pictured above during his time working on the RINGS project) to have a novel experience of research and technology development not easily available during their undergraduate degrees.

The current CARES small projects include: Development of Multi-Step Processes in Pharma (funded by the private-public partnership, Pharmaceutical Innovation Programme Singapore PIPS), RINGS (funded by SMART Innovation Centre) and Intelligent Platform for Efficient Energy Management (a collaboration with E2S2 and NUS under the Intra-CREATE seed fund).

There are also ten new projects under the C4T Emerging Opportunities Fund, started to support exciting new ideas that have arisen since the start of C4T Phase 2.

Development of Multi-Step Processes in Pharma
With funding from Pharma Innovation Programme Singapore (PIPS)

This project is funded under the Pharma Innovation Programme Singapore (PIPS) programme and led by Prof. Alexei LAPKIN. This is a three-year project with S$1.8m budget, and formally commenced on 16th June 2019.

For a given active pharmaceutical ingredient (API), the complexity of the multi-step chemical synthesis and purification, and the enormous number of possible reagent and reaction condition combinations are significant bottlenecks for rapid large-scale manufacturing. The work conducted by Dr Simon SUNG (Research Fellow) and Mohammed JERAAL (Research Associate) at Cambridge CARES is focused on developing a novel automated self-optimising system that can rapidly identify sustainable and high yielding multi-step chemistry and purification routes in tandem. This will be achieved by combining programmable chemical handling equipment, analytical tools and machine learning (ML).

With greater experience in chemistry, Dr Simon SUNG has led a study on identifying impurities for a given synthetic route. Importantly, the robustness of a given preparation route (synthesis and purification) is significantly defined by the impurity profile produced. As such, gathering information either through the literature or through experimentation has been the primary focus of the chemistry work recently. This information will be provided to the automated self-optimising system being developed, which was described in the previous report, to ensure that the final optimised route produces manageable quantities of easy-to-remove impurities and is suitable for scaling up to large scale synthesis. This impurity factor will be optimised simultaneously alongside other targets such as space-time yield, cost, and EcoScore.

Through a combined effort by both Dr Simon SUNG and Mohammed JERAAL, a suite of python-based user interfaced applications has been written to aid the chemical process development in our project. From relatively simple applications such as (i) for calculating our in-house developed EcoScore for any chemical, (ii) identifying suitable industrially relevant reaction solvents based on their properties, (iii) and automated flow chemistry HPLC-UV calibration of analytes, (iv) to a significantly more complex application for controlling and monitoring our self-optimising, machine-learning, multi-step synthetic and purification system.

For more information on this project, see Simon and Mohammed's 'Focus on Fundamental Science' article on page 14.

An Intelligent Platform for Efficient Energy Management in an Eco-Industrial Park
Intra-CREATE seed grant

The Intra-CREATE Seed Collaboration project "An Intelligent Platform for Efficient Energy Management in an Eco-Industrial Park", a collaboration between National University of Singapore (NUS) and CARES, commenced on 1 March 2019. The project aims to develop a platform for efficient management of energy production and consumption in an Eco-Industrial Park (EIP). Due to COVID-19 the end date of the project has been extended to February 2021. However, spend in CARES had completed by the original planned end date of August 2020. The work on this project during the no-cost extension period is therefore primarily happening in the Host Institution, NUS, with inputs from the CARES PI (Prof. Markus KRAFT).

Rapid Industrialization of Next Generation Nanomaterials
With funding from the SMART Innovation Centre

The goal of the RINGs project (Rapid industrialization of next generation nanomaterials) is to develop and commercialise scalable processes for advanced nanomaterial synthesis. In this project, co-funded by the SMART Innovation Centre and led by Dr Nicholas JOSE (Research Fellow, CARES), continuous microreactors, machine learning and automated methods are being combined as a platform for materials development and scale-up. The proof-of-concept project is the rapid development of antibacterial nano-ZnO coatings.

An article summarising the RINGs work was recently submitted. Kg/day scale production was achieved in a microreactor with high antimicrobial efficiency. The complexity of scale-up was significantly reduced through the use of our microreactor and machine learning for multi-objective optimisation. Process efficiency was up to 100x better than previously published methods and used room temperature conditions. Dr Nicholas JOSE is working on commercialising this material and process with industrial collaborators. An automated rig for reactions has been developed and tested in the CARES lab for continuous production, and a large-scale automated rig for up to 50 kg/day production is also under construction.

Work is also continuing on the development of high capacity electrodes for supercapacitor and batteries. A new intern from NUS, Marsha HU-MAIRA, has been helping with the fabrication and testing of new formulations.

An application has been made, with the support of NTUitive, to the Central Gap Fund for further development of the commercial potential.
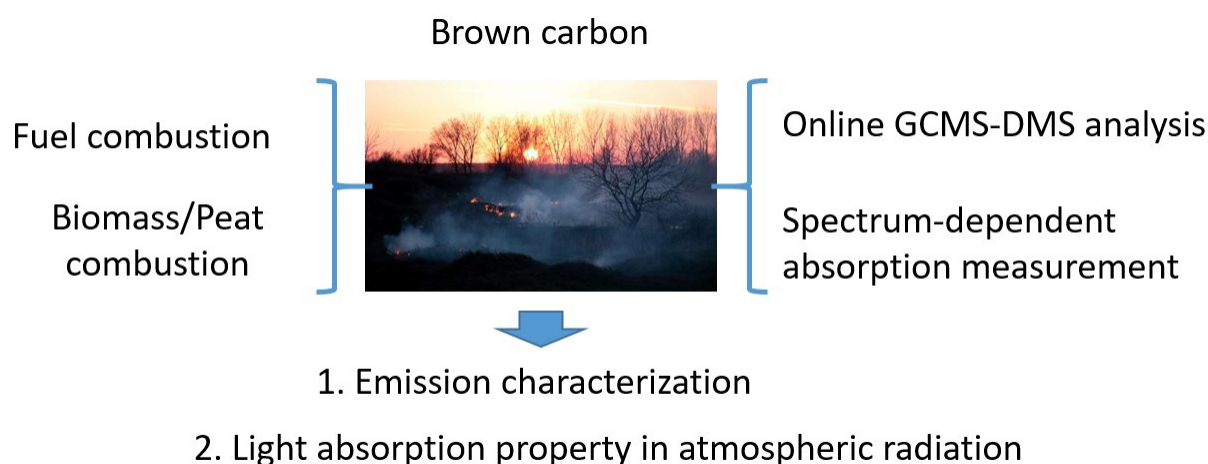
C4T Emerging Opportunities Fund

1) Brown carbon laser characterisation and light-absorbing property

Prof. Markus KRAFT and Dr Yichen ZONG

Brown carbon (BrC, light-absorbing organic carbonaceous species) has attracted strong concern as a possible cause of climate change and a major air pollution source in Southeast Asia. In this study, we will investigate the characterisation of combustion emissions from diesel, biomass and peat by measuring the chemical composition, number concentration and size distribution. An optical method (multi-wavelength light absorption) will be used to distinguish brown carbon from all other organics and black carbon emission. An estimation of absorption properties will be performed to evaluate the role of brown carbon in atmospheric radiation balance.

The experimental work of the project is ongoing since the lab has reopened. In collaboration with external researchers from NUS Environmental Engineering, we tested three primary transportation fuels (diesel, jet fuel A-1, marine oil) in the single cylinder engine. The aerosol light absorption was measured by using a seven-wavelength aethalometer (model AE33). AE33 is a standard instrument for light absorption study in climate research and is provided by our collaborator. In the experiments, low engine loading cases show a higher ratio of BrC/BC and large amount of organic species are also detected by SP-AMS. More experiments will be conducted this year under different combustion conditions to study the growth environment of brown carbon.

Brown carbon

Fuel combustion

Biomass/Peat combustion

Online GCMS-DMS analysis

Spectrum-dependent absorption measurement

1. Emission characterization
2. Light absorption property in atmospheric radiation

2) Chemical farming

Assoc. Prof. YAN Ning, Prof. Alexei LAPKIN, Dr Zhen GUO and Dr Song SONG

This projects targets establishment of chemical routes to convert woody biomass components into value-added amino acids and other nutrients to replace the slow, ineffective biological pathways in nature. Along this line, we started to develop new pathways to synthesise proline, tyrosine and glucosaminic acid. Meanwhile, through adoption of molecular similarity approach and fine-tuning the search algorithms on the basis of Reaxys database, we are able to search for most

useful sub-structures that are identified in the bio-waste sources and linking these sub-structures with reaction networks data.

A key target of the project is to make amino acids from renewable feedstock. We intend to develop new catalysts and catalytic systems to construct amine groups in amino acids. Recently, a new research fellow, Dr Shipeng DING, has started working in the project. While most reported sys-

tems rely on Ru nanoparticles are active sites, he is developing new Ru-based, single-atom catalysts to conduct reductive amination reaction which may be more selective than nanoparticles. In the past months, we utilized two Ru organometallic precursors and doped them on TiO_2 rutile, ZrO_2-tetragonal and ZrO_2-monoclinic supports, and treated the catalysts at 200 ˚C. The series of six catalysts have been characterized by CO-DRIFT IR technique. Peak at 2026 cm -1 suggests CO adsorption on Ru nanoparticles, where-as peaks at 2050 and 2000 cm-1 highlights dicarbonyl species Ru $\delta+$ (CO) 2. Peak at 1980 cm -1 indicates CO adsorption on oxygen vacancies of RuO_2 . Using these criteria, we confirmed that two of the six catalysts have atomically dispersed Ru species on the surface. In the next stage, we will use X-way absorption spectroscopy and TEM techniques to collaborate IR findings. We will also evaluated the activity of these catalysts in reductive amination reaction to identify structure-activity correlations.

3) Impact of Singapore's shipping activities on urban air quality

Prof. Markus KRAFT, Mei Qi LIM and Jiaru BAI

In this project, we propose to develop a framework to evaluate the impact of emissions from shipping activities on air quality in Singapore by combining physical-based model with data-driven model based on morphology and real-time data such as marine traffic and weather conditions. Jiaru Bai (PhD student, University Of Cambridge) has extended the domain ontology for combustion engines, OntoEngine, to include the capability to semantically represent data obtained from measurement campaigns on engine test rigs. This extension is necessary as existing ontologies are very coarse and high-level, with insufficiently detailed concepts to be suitable for our purpose i.e. to capture data as produced by commercially available engine test stand software that is being used in industrial practice. The design of the ontology also encompasses input quantities required by the SRM Engine Suite, a virtual engineering design tool based on a Stochastic Reactor Model (SRM) engine simulation code that is capable of internal combustion engine performance and exhaust gas emissions prediction using detailed chemical models. The OntoEngine ontology defines 67 classes, 65 object properties, and 34 data properties. As a graph, this corresponds to 102 nodes and 151 edges. The ontology has been structured specifically to represent data in a storage efficient manner as they are typically recorded in engine measuring campaigns. In addition, in collaboration with IRP4 and IRP JPS, we are jointly developing physical-based models for atmospheric dispersion by using an extended urban dispersion model called "EPISODE-CityChem", to evaluate its suitability for simulating atmospheric dispersion of shipping emissions. We have also been working on consolidating and restructuring pre-existing components according to the current architecture. This work involved packaging the pre-existing components as agents that can apply the semantic web stack to read and understand information from the knowledge graph and modify its data values.

4) Ignition systems and methane slip in marine natural gas engines
Prof. Epaminondas MASTORAKOS

The aim of the project is to perform simulations of the methane slip and ignition mechanism in pilot-ignited and jet-ignited natural gas marine engines. The work will be based on the Large Eddy Simulation paradigm supplemented with the recently-developed Doubly Conditional Moment Closure subgrid combustion model.

Hiring issues have caused some delay to the project. Some preliminary work in the jet ignition system has been performed by the PI: a Direct Numerical Simulation dataset published in the open literature is being analysed from the perspective of the fundamentals of the Doubly-Conditioned Moment Closure, which will form the basis of the project, to give a head start to the new post-doc.

5) Future marine economy
Prof. Epaminondas MASTORAKOS, Prof. Steve EVANS

The decarbonisation of the shipping sector is inevitable, but also one of the most difficult to achieve, with various options being discussed such as batteries, hydrogen, ammonia and biofuels. Each of these energy carriers has different costs, sources, carbon footprint, and technology readiness level.

Inextricably linked to energy use in marine transport is a consideration of the emission of other pollutants that have an adverse health effect at the local scale. The amount of pollutants such as NOx, SOx, soot, VOCs may change as technologies develop or oil is displaced. Switching fuels may also affect climate change in unexpected ways, for instance the greenhouse gas potential of CH4 slip from LNG ships may negate the CO2 reduction benefits. Predictions of which technologies may dominate are currently poor, while the choice will have profound impacts on Singapore air quality, energy plan and policy and port and industrial policy.

The post-doctoral researcher for this project has not been selected yet. Important preliminary work has been performed by Beatrice Foscoli, a visiting Masters student, who analysed from a lifecycle analysis perspective the energy and CO2 emissions associated with various options of alternative marine fuels and what this means for Singapore's bunkering activities and electricity generating capacity. The alternative bunkering fuels studied were electricity, hydrogen, ammonia, methanol, biodiesel, and LNG, with hydrogen and ammonia ("e-fuels") produced by electricity. The extra amount of energy and the reduction of CO2 emissions have been quantitied. Biofuels may be a suitable solution for shipping decarbonisation, given the abundance of woody biomass in South East Asia and e-fuels could result in significant reductions inCO2 emissions, if the electricity is carbon-free. The extra electricity capacity needed for each of these options has been shown to be many times the current installed in the Singapore electricity grid, which implies significant investments in electricity generation and in LNG import (for the short term) or renewable energy (for the longer term) must be made so as to decarbonise Singapore's contribution to world's shipping fuelling.

6) Carbon reduction strategies of top chemical companies

*Prof. S. VISWANATHAN, Dr Abhiruchi GADGIL, K. R. Preethi*

The purpose of this research is to understand the current (articulated) concerns related to sustainable operations among top chemical manufacturing and oil and gas companies in the world, as well as the strategies, technologies and practices being adopted by them to mitigate CO2 emissions and other environmental externalities generated by their operations. The main data sources being used for this empirical research work are sustainability (ESG) reports published by the top 50 companies in the aforementioned industrial sectors, media articles in the industry and business press, key reports from international environmental organisations as well as commercial databases.

We have commenced work on the EOF proposal for understanding articulated concerns of top CO_2 emitting companies in the implementation of low-carbon initiatives. The current study is to understand carbon reduction strategies for top oil and gas companies.

It will be followed by chemical manufacturing, steel and cement companies. A varied data has been gathered from various sources including GRI reports, intergovernmental agencies, consultancies, think tanks and consortiums for the oil and gas sector. We have understood the gaps in the publicly available data and will be procuring some commercial databases to have comprehen-

sive datasets. The study is aiming to decipher different factors that can affect the carbon reduction measures. The approach of the study includes technological (low-carbon R&D, patents, emissions reporting and mitigation measures), strategical (investments and divestments towards low-carbon future) and financial (carbon tax carbon pricing, tax credits) considerations. The oil and gas sector is in a big flux due to COVID, and this possibly might add another dimension to the study in terms of understanding strategic priorities through crisis.

For the EOF work specifically on carbon pricing, we have been working on how internal carbon price needs to be designed at a large multi-unit firm. When the abatement cost structure is strictly convex, it shows that a uniform tax achieves the first-best solution. However, in the long term, a non-uniform tax is recommended, to ensure that the current businesses stay alive. Currently, we are examining other abatement cost structures. This is for scenarios when there is a linear abatement cost and single carbon tax is inefficient and is not the first-best solution. For this, we have proposed to use a stepwise tax structure, which enables the firm to exactly achieve its emission target. The computational results are underway and the results are being drafted to be included in a new manuscript for submission to a journal.
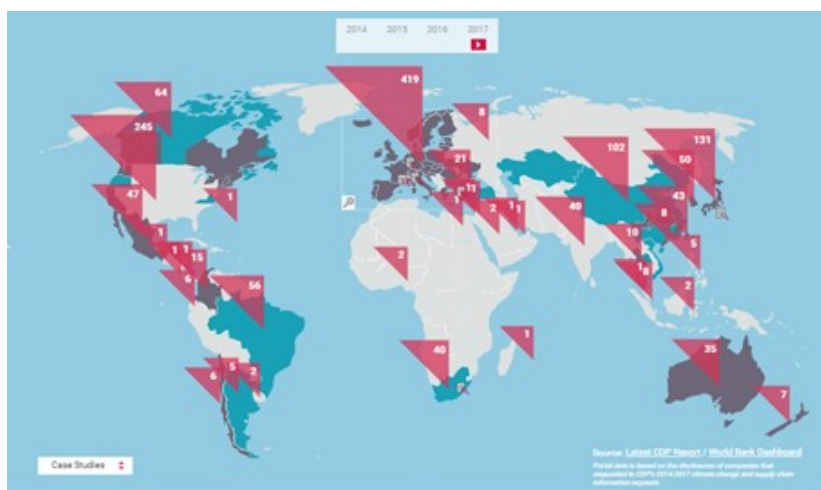
Nearly 1400 companies use some form of internal carbon pricing in their operations, which is an eight times increase in a four-year time period.

Image Courtesy Carbon Disclosure Project (CDP)

7) Carbon capture, storage and utilisation roadmap 2050

Asst Prof. Paul LIU, Prof. Markus KRAFT

In this roadmap study, we will take a retrosynthetic approach to identify the research intensity and the scaling-up milestones required to achieve the 2030 and 2050 emission reduction targets by CCSU, the former is linked to Singapore's pledge following the Paris Agreement whilst the latter will be addressed by our analysis. Firstly, the decarbonisation potential of the various emission reduction approaches, including improved power plant efficiencies (e.g. CCGT, co-gen and waste-to-energy plants), improved grid efficiencies and improved user efficiencies (e.g. building efficiency, green manufacturing, etc), circular economy, renewable power generation (primarily by PV, in the Singapore context) and CCSU will be evaluated. Secondly, the major point-sources of emission will be paired with the market demand for purified CO_2, carbonaceous fuels, solidified carbon (e.g. carbonates and biochars), and downstream chemical products (e.g. olefins and liquid fuels), to develop a carbon circular supply chain. Then, by developing process models and financial models for the various key CCSU plants (e.g. CO_2 to methanol, power to liquid, carbon aggregate production), the levelised cost of manufacturing products via CCSU can be estimated. Overall, the multi-scale model will enable the evaluation the cost-effectiveness of the proposed carbon circular economy, which will be compared against the fossil-fuel driven economy. We anticipate the modelling results to show that the carbon circular economy, as the current technologies stand, compares unfavourably to the fossil-fuel based economy from a financial point of view.

Pandemic-related hiring delays have slowed progress on this project, but PIs are currently exploring various options to deal with the shortage in manpower.

8) Designing the structure and composition of active site motifs in CO_2 hydrogenation catalysts with atomic-level specificity

Asst Prof. Paul LIU, Prof. Alexei LAPKIN, Asst Prof. Tej CHOKSI

The overall objective of this project is to build operando-computational models for bifunctional Cu/CeO_2 interfaces by closely integrating theory with precisely targeted characterisation and kinetic experiments. Successes in this effort will establish quantitative capabilities for determining both structures of bifunctional interfaces under reaction conditions, and CO_2 hydrogenation kinetics with atomic level specificity. We will then deploy these models for the high-throughput design and validation of thermodynamically feasible active sites of physically and chemically modified Cu/CeO_2 interfaces that demonstrate superior rates and selectivity towards methanol. The central hypothesis of this proposal is that bifunctional gains observed in the rates and selectivity of CO_2 hydrogenation are induced by electronic interactions between the metal and the oxide support.

We investigated the structures and adhesion energies of Cu films with different thickness supported on CeO_2 using Density Functional Theory (DFT) calculations, with the aim to get insightful understanding on the charge transfer and oxidation-reduction interactions between the metal and oxide. However, due to the complications arising from the charge transfer between Cu and Ce atoms at the contacted interface inducing the formation of Ce^{3+} site, the magnetic moment for those specific Ce sites will need to be set very appropriately to ensure the convergence of the DFT calculations. We have managed in developing the workflow to carefully converge the electronic structure based on the ramping procedure. Future works will evaluate the adhesion energy of Cu layers on different exposed facets of CeO_2, as well as consider the influence of oxygen vacancies, co-adsorbate and strain effects to the Cu adhesion energy. Based on those obtained results, we would then be able to theoretically predict the morphology of supported Cu on CeO_2 under realistic conditions and perform the kinetic study for reactions on those Cu/CeO_2 catalytic systems.

9) Electrified chemical production: AI strategies for accelerated intelligent design of disruptive technologies and electrochemical processes

Prof. Jason XU Zhichuan, Dr Adrian FISHER, Dr Chen GAO

This project aims to develop the machine learning methods for electrocatalysis and longer term reactor engineering design. We will first build the database of various catalyst materials and their related catalytic performance for training purposes. The machine learning models will be built on the basis of the fundamentals discovered. The models will be further optimised by incorporating more data sets, such as materials' physical and chemical parameters. DFT simulation will be employed for experimental data mining as well as the validation of machine screened catalysts. Finally, the machine designed catalysts will be synthesised and tested to confirm the successful design. We propose to develop our computational strategy and use it for proof of concept for target reactions in the area of small molecule transformations. Targets would include hydrogen production (water oxidation), C1-C4 molecule transformation, high value chemicals, and high energy consuming products such as nitrogen oxide, etc.

Significant progress has been made on combining density functional theory (DFT) calculations and machine learning methods to fast screen highly active oxygen evolution reaction (OER) spinel catalysts. Inspired by the finding that the OER activity on spinel oxides is intrinsically dominated by the covalency competition between tetrahedral and octahedral sites, a dataset with more than 300 spinel oxides is computed and employed to train a machine-learning model for screening the covalency competition in spinel, with a mean absolute error of 0.05 eV. Meanwhile, $[Mn][Al_{0.5}Mn_{1.5}]O_4$ is predicted computationally and further confirmed experimentally to be a highly active OER. This work provides design principles of spinel oxides for OER. In addition, we have also investigated the alkaline hydrogen evolution reaction (HER) activity at a series of NiCu bimetallic surfaces, where the electronic structure is modulated by the ligand effect. The HER activity shows a correlation with either the calculated or the experimental-measured d-band center via a volcano-type relationship, suggesting the descriptor role of the d band center. This work may offer an insightful understanding of alkaline HER, and longer-term catalyst design.

10) Construction of isolated metal sites for selective electrocatalytic production of H_2O_2

Prof. WANG Xin

Hydrogen peroxide (H_2O_2) is one of the most important chemicals, being widely used in almost all industrial areas with an annual demand of 4 million tons. H_2O_2 is currently produced almost exclusively with the anthraquinone oxidation process. However, the anthraquinone technology involves multistep reactions and separations, which require significant energy input and generate substantial waste. Electrochemical strategy via the oxygen reduction reaction (ORR) process provides a promising approach to achieve the low-cost, green, continuous and on-site production of H_2O_2, making it a simpler and safer method compared with the conventional anthraquinone process. This research aims to develop a novel and low cost catalyst and reactor system to efficiently produce H_2O_2.

We have gone through the recruitment process and identified two candidates. Due to COVID-19, the earliest time that they can land in Singapore is 6 months later. To mitigate this delay, Dr LI Xiaogang, who was previously supported by C4T and is currently supported by other funds, has helped to kick-start the project. Some progress has been made. We developed a molecular strategy to modulate the NiN_x sites towards electrocatalytic reduction of O_2 to H_2O_2. The anthraquinone -based molecule was fixed on the NiN_x catalysts through π-π interaction. Benefitted from the unique structure of NiN_x sites, the electrocatalyst shows a higher onset potential for H_2O_2 production, indicating the low overpotential for O_2-to-H_2O_2 conversion. Meanwhile, the anthraquinone molecule effectively suppresses the further dissociation of intermediate, resulting in the high selectivity for the O_2 reduction towards H_2O_2.

PUBLICATIONS

ALL C4T PUBLICATIONS WITH CREATE ACKNOWLEDGEMENT

The following list includes all the C4T publications from the beginning of Phase 2 (November 2018). Those in bold are new for this reporting period. 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

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