Unconventional Methods in Chemistry Workshop

Monday 30 October
9am - 12:40pm (SGT)

Pinnacle Room L16,
CREATE Tower, NUS

9am - 9:10am Introductory Remarks

9:10am - 10am "Alternative technologies for the selective conversion of bio-based feedstocks to specialty chemicals"
Prof Francois Jerome; CNRS Research Director

10am - 10:25am "Carbon-Negative Generation of Green Hydrogen via Electrolysis of Biomass"
Assoc Prof Hong Li; NTU

10:25am - 10:50am "Design of Efficient and Durable Oxygen Evolution Reaction Catalysts"
Prof Xu Rong; NTU

10:50am - 11:10am Tea break with refreshments

11:10am - 11:35am "Mechanochemically-Driven Chemical Conversion"
*Dr Amol Amrute; Institute of Sustainability for Chemicals, Energy & Environment (ISCE2); A*STAR*

11:35am - 12pm "Low Temperature Nitrogen/Carbon-plasma Engineered High-performance Electrocatalytic Electrode Materials"
Prof Rajdeep Singh Rawat; NIE/NTU

12pm - 12:25pm "The mechanism, kinetics, and role of OH radicals in ultrasound-mediated aqueous organic oxidation chemistry"
Dr Ari Fischer, Research Fellow; NTU

12:25pm - 12:40pm Closing Remarks

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Alternative technologies for the selective conversion of bio-based feedstocks to specialty chemicals

Prof Francois Jerome; CNRS Research Director

With the growing concerns of our society about climate change, a strong political impulsion has been given to the defossilisation of our industry. In this context, the production of chemicals from biomass waste (sugars) has become of particular interest. The chemical activation of sugars generally requires heat which unfortunately lead to uncontrolled degradation reaction and the formation of side products. In terms of selectivity issue, being able to activate sugars at low temperature is a prerequisite, but remains difficult. The massive electrification of our society now opens rooms for the development of alternatives technologies, in particular to replace the tradition “chemical” by a “physical” activation. We will illustrate this possibility by discussing the mechanocatalytic synthesis of biosurfactants directly from cellulosic biomass. The impact of water and minerals present in biomass on the mechanocatalytic process efficiency will be discussed as well as a life cycle assessment to shed light on the contribution of this technology as compared to the current industrial process. Turning now to reactions in water, an essential solvent for biomass, we will highlight the contribution of ultrasound for the catalyst free biomass processing. We will show that high frequency ultrasound is capable of generating •OH radicals (homolytic dissociation of water inside cavitation bubbles), and thus to initiate chemical reactions at a nearly room temperature with sugars. Transposition of this technology for the activation and conversion of NH_3 (future H_2 carrier) will be also discussed, particularly for the metal free hydrogenation of biobased alkenes in water.

Design of Efficient and Durable Oxygen Evolution Reaction Catalysts

Prof Xu Rong; NTU

Production of hydrogen by water electrolysis using renewable energy is a promising technology towards sustainable energy future. However, at this stage, it cannot compete with the conventional methane steam reforming process in terms of technoeconomics. Among a number of obstacles to its practical application, the sluggish kinetics of the oxygen evolution reaction (OER) at the anode of water electrolysers has drawn the most attention. Enormous efforts have been spent to develop OER catalysts with a lower overpotential using earth-abundant elements, in pursuit of higher energy efficiency and lower capital cost. In this regard, more degrees of freedom in catalyst design are available for alkaline water electrolysis where the electrochemical environment on the anode is milder than in proton exchange membrane water electrolysis and high-temperature water electrolysis. Conventionally, the activity of water-splitting catalysts is compared by the overpotential at the current density (j) of 10 mA cm^{-2}. Practical water electrolysers operate at current densities that are 1–2 orders of magnitude higher and demand long-term stability in addition to a low overpotential. As representatives of low-cost OER catalysts, Fe, Co, and Ni form the basis of industrial alkaline water electrolysers. In this talk, various strategies in designing efficient and durable OER catalysts will be discussed through a few recent examples studied in our lab.

Carbon-Negative Generation of Green Hydrogen via Electrolysis of Biomass

Assoc Prof Hong Li; NTU

Alkaline water electrolysis is the most promising technology for large-scale production of renewable hydrogen. Howvever, the cost of the generated hydrogen is limited by the cost of electricity used to drive the electrolyser. To reduce the cost, one can employ renewable energies (such as PV or wind), however current sources are too intermittent to be compatible with alkaline water electrolysis. To date, the issues of hydrogen and oxygen gas mixture, especially at partial loading, and sluggish kinetics of oxygen evolution reaction (OER) have not been effectively addressed. Recently, the proposal of using redox mediators, as a replacement of OER, to decouple hydrogen evolution reaction (HER) spatially and temporarily, received ever-increasing attention. The decoupling strategy increased operation safety but not necessarily decreased the cost. Although a series of organic molecules oxidation were reported to replace OER, the low scalability of the new oxidation reaction greatly limits its commercialisation potential. To solve the scalability issue, we use abundant biomass oxidation reaction (chitin oxidation) to replace sluggish OER in alkaline water electrolysis. Chitin, the most abundant amino biopolymer with 100-billion-ton annual production in nature, was selectively transformed to acetate on the anode, without gas product formed. When coupled with hydrogen production on the cathode, energy consumption can be saved with safer operation. The selectivity of chitin to acetate can also reduce the overall cost by simplifying the separation. Most importantly, the reactant on the anode (chitin) is abundant enough to scale up with that on the cathode (water), making the new redox couple as scalable as the HER-OER couple in traditional water electrolysis. Moreover, I will share our work on other abundant waste besides chitin. Our hybrid alkaline water electrolysis thus removes the safety issue from explosive gas mixture, and be driven by renewable energy such as solar energy for cost-effective production of renewable hydrogen.

Mechanochemically-Driven Chemical Conversion

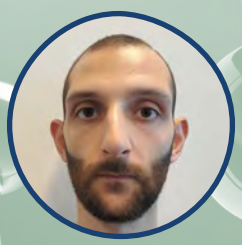
*Dr Amol Amrute, ISEC2; A*STAR*

Mechanochemistry enables chemical reactions under milder conditions than thermochemical methods and even without solvent, making it a greener route for chemical conversion. Due to these features, mechanochemistry has recently received noteworthy interests from different fields of chemistry, including materials and catalysis. In the latter area, mechanochemistry has not been limited to the synthesis of materials/catalysts, leading to properties that are normally unachievable by conventional methods, but it has also been reported as a very effective tool for performing catalytic reactions with exceptional performance. In this talk, I will discuss how mechanical forces lead to chemical reactions and what effects they cause to materials or chemicals. In particular, the presentation will cover the mechanochemical synthesis of catalytic materials, with examples of the room-temperature synthesis of nano-corundum (and its application in Fischer-Tropsch synthesis catalyst design and use as robust methanol dehydration catalyst), hybrid materials, and catalytic reactions of small molecules under the influence of mechanochemical force.

Low Temperature Nitrogen/Carbon-plasma Engineered High-performance Electrocatalytic Electrode Materials

Prof Rajdeep Singh Rawat; NIE/NTU

The focus of this talk will be on fabrication of 3-D porous nanostructured anode electrode materials for water electrolysis using low-temperature nitrogen or carbon plasmas as an alternative novel method which is cost-, time- and energy-efficient. Currently, the research and development in wet chemistry dominates the synthesis and processing of anode electrode materials. Innovative and environmentally friendly synthesis and processing technologies for development of new materials with desired structural, morphological, physical and chemical properties are actively being explored. Plasma based material processing and synthesis is one such attractive alternative technology. The electric discharges in gases produce excited high-energy electrons which in turn produce energetic environments rich in free radicals and high-energy particles which can disrupt existing chemical bonding or generate new chemical bonds on electrocatalytic so that some thermodynamically or kinetically unfavorable reactions and formation of defects on materials' surface can be achieved. Plasmas thus produce multi-dimensional defects on nanomaterials and add active sites for a variety of electrocatalytic processes improving their performance and even stability. The energy and matter exchange between plasma and materials provides a versatile platform for surface functionalisation and energetic ions induced sputtering can change the surface structure and morphology. We have used low-temperature non-thermal nitrogen/carbon-plasma-based synthesis and processing strategy as a novel tool for the preparation of advanced porous 3-D nano-assemblies that provide electrode materials with excellent charge transport, low overpotential, and high-stability. In this proposed talk I will provide the overview of the work done on using low temperature nitrogen/-carbon plasma in RF-PECVD system to process, functionalise, and nano-structurise electrode materials to significantly improve electrocatalytic performances.



The mechanism, kinetics, and role of OH radicals in ultrasound-mediated aqueous organic oxidation chemistry

Dr Ari Fischer, Research Fellow; NTU

Sonochemical processes drive aqueous reactions of organic solutes into valuable products by leveraging the ability of ultrasound to generate free radicals. Using water as a solvent and electricity as a power source, ultrasound promises a path for renewable and sustainable chemistry. Computational modeling and kinetics experiments are combined here to understand the mechanism behind ultrasound-driven oxidation of aqueous glyoxal, a C_2 di-aldehyde commonly formed by oxidising larger organic molecules, to form glyoxylic, oxalic, formic acids, and CO_2. The mechanistic insights gleaned here reveal experimental conditions that favour selective formation of C_2 products while preventing undesired C-C cleavage to C_1 products. These results demonstrate that ultrasound-driven reactions can be controlled and made selective towards desired products by understanding the relevant chemistry at play and tuning the reaction environment accordingly.