

ABSTRACT BOOK

DAY-01

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**Session: JST-ERATO Special Session: Australian Science and Technology
(Broadcasting to the JST-ERATO Center Venue)****Biomimetic Nanostructures Materials Controlling Cellular Activity****Alan E. Rowan**

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Fibrous networks of biopolymers are found in both the intracellular and extracellular matrix. From the microscopic scale of a single cell to the macroscopic scale of fibrous tissues. Biopolymers with different stiffness control cellular processes such as cell differentiation, proliferation, transportation and communication. In recent years, a large number of different hydrogels has been developed, often with the goal to create an artificial extracellular matrix for biomedical applications. However, the mechanical environment inside and outside the cell is not determined by a single component. Multiple interpenetrating biopolymers with different structural and mechanical properties physically interact with each other, finely tuning the mechanical environment of a cell *in vivo*.

The mechanics and physics of natural biopolymer gels however are very different from most synthetic hydrogels because they show strain stiffening behaviour. Reconstituted networks of cytoskeletal polymers such as actin or intermediate filaments or extracellular biopolymers such as collagen or fibrin show a large increase in stiffness upon an applied stress or deformation. The stiffening response is a result of their nanostructured and prevents from breaking under external stresses and enables communication between cells growing in these materials.

Our efforts to synthesis genuine biomimetic polymer hydrogel with unique materials properties almost identical to these of intermediate filaments and extracellular matrices and approaches to controlling natural fibre networks properties will be discussed. The critical role of nonlinear mechanical properties in controlling cellular behaviour and the potential for smart nanomaterials will be discussed.

Engineering Metal–Organic Materials via Supramolecular Assembly**Frank Caruso^{a,*}**

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The development of rapid and versatile coating strategies for interface and particle engineering is of widespread interest. This presentation will focus on our studies on the formation of a versatile class of metal–organic materials, metal–phenolic networks (MPNs), which can be formed on various substrates by coordinating polyphenols and metal ions through self-assembly. This

robust and modular assembly strategy is substrate independent (covering organic, inorganic, and biological substrates) and has been used for the preparation of various materials, including thin films, particles, superstructures and macroscopic assemblies. It will be shown that a range of polyphenols and a library of metal ions are suitable for forming MPNs. The MPN materials are stable at physiological pH but disassemble at acidic pH, thus making them of interest for the intracellular release of therapeutics. By altering the type of metal ions, different functions can be incorporated in the MPN materials, ranging from fluorescence to MRI and catalytic capabilities. Furthermore, synthetic polymer–phenol conjugates have been used as building materials to control the biofouling properties of the MPN materials. Examples of self-healing MPN gel materials and engineered protein-based nanoparticles will also be highlighted. The ease and scalability of the assembly process, combined with the tunable properties of MPNs, provide a new avenue for functional interface engineering and make MPNs potential candidates for biomedical, environmental, and advanced materials applications.

Designing Electrode Materials and Electrolyte for Metal-Ion Batteries

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Energy storage is essential to realize low carbon society and there have been many challenges. Alkali metal ion batteries, especially Lithium ion batteries and sodium ion batteries are particularly attracted attention of scientists and engineers as promising devices. Materials engineering plays a key role in the field of battery research. In particular, engineering materials at the nanoscale offers unique properties resulting in high performance electrodes in various energy storage devices. Consequently, considerable efforts have been made in recent years to fulfill the future requirements of electrochemical energy storage devices. Various multi-functional hybrid electrode materials and electrolytes are currently being studied to improve energy and power densities of next generation batteries. In this talk, I will present some of our recent progress in the synthesis of different types of hybrid electrode materials and electrolytes to enhance the electrochemical energy storage properties of metal-ion batteries ^[1-4].

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Nanomaterial Properties Analyzed in an Electron Microscope

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The unique usefulness of diverse state-of-the-art in situ/operando high-resolution transmission electron microscopy techniques for the detailed property analysis of a wide range of advanced inorganic nanomaterials, e.g. nanotubes, graphene-like nanosheets, nanowires, nanoparticles, nanocomposites and heterostructures is demonstrated. The Young's modulus, tensile strength and strains to fracture, electrical conductance and nanotube transistor performance,¹ thermal flow gradient, photocurrents,² photovoltages and spatially resolved cathodoluminescence of advanced nanomaterials are unambiguously determined under the highest spatial, energy and temporal resolutions inside the electron microscope, while employing piezo-driven electrical probes, mechanical sensors, nanomanipulators and optical fibers assembled within the microscope column.

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Session: Energy and Environmental Materials

Investigating Battery Electrode Materials Operating via the Alloying-dealloying Mechanism

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Carbon negative electrode materials (graphite and hard carbon) enable the most common concepts of metal-ion (Li, Na, K) and dual-ion batteries. These materials have attractive electrochemical performances but limited theoretically available capacity (e.g., 372 and 278 mAh/g for graphite upon lithium and potassium intercalation, respectively). A different class of negative electrode materials that include Si, Bi, P, Sn, Sb, Al exists as an alternative to graphite and hard carbon and offers considerably larger capacities. Among these materials, Si is on the brink of commercialisation in lithium-ion batteries and other elemental and cross-alloyed phases are actively analysed in research groups.

Selected results on the experimental discovery and application of alloying materials in batteries will be discussed in the talk. In particular, the use of Sb and black phosphorus in sodium-ion batteries [1, 2], the initial studies on Sn and black phosphorus in potassium-ion batteries [3, 4] and the fabrication of full cells with alloying-based anodes in the form of dual-ion batteries [5] will be covered. In order to optimise performance, the materials in all examples are synthesised as composites of the corresponding phases with a carbon co-component.

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Study on Smelting Metal by Microwave Irradiation

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Chemical reactions under microwave irradiation are characterized by high reaction rates, selective heating, and low reaction temperatures and are thus being studied to elucidate the phenomena. In particular, materials such as scandium and magnesium are expected to reduce greenhouse gas emissions by reducing the weight of the transportation equipment and can also be used as materials for communication equipment. We performed the reduction of magnesium and scandium oxides and proved that they are more efficient than conventional methods [1–3]. In these reduction reactions, a decrease in reaction temperature was observed, and the involvement of plasma in the microwave-assisted process was indicated [4]. It was also noted that equipment comprising multimode microwave applicators, which has been used in many studies, is not suitable for industrial applications because of the difficulty in scaling up the size of the equipment. Therefore, to elucidate the phenomenon and to make the device larger, experiments were conducted on the generation and reduction reaction of magnesium plasma using a cylindrical transverse magnetic (TM)-mode applicator in magnetic field mode (TM110) and electric field mode (TM010). As a result, by heating Mg powder using the magnetic field mode TM110, plasma was generated with the evaporation of Mg and then stably sustained. Conversely, in the electric field mode, plasma was generated but was unstable. When the Mg plasma sample was introduced into the reaction zone and exposed to lamp heating, it was observed that the reduction reaction of scandium oxide also occurred. The results of this study provide a prospect for the development of a larger microwave refining system.

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Advanced Materials for Non-aqueous Aluminum-ion Batteries

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The development of efficient energy storage systems is of urgent need in modern society, motivated by the expansion of renewable energy and the growing demand for electric vehicles and mobile devices. Combined with safety and sustainability concerns, current research interest has shifted towards safer and more earth-abundant materials in order to replace lithium-ion battery systems. Aluminium ion batteries (AIBs) have emerged as one of the most promising alternative energy storage technologies because of their high volumetric capacity (8040 mAh cm⁻³ for Al vs. 2046 mAh cm⁻³ for Li) and abundant aluminium reserves for large-scale electrical energy storage. Many types of cathode materials have been developed so far, including carbon materials, metal dichalcogenides and phosphides. Carbon materials are prone to deliver high operating voltage and long cycling life, however, show limited capacities due to the sluggish intercalation/de-intercalation processes of large-sized AlCl₄⁻ anions. Regarding transition metal-chalcogen compounds, although they are reported with higher capacities than carbons, the materials suffer from capacity fading caused by irreversible phase transfer and even destruction of the original lattice during Al³⁺ intercalation. Therefore, the lack of suitable cathode materials with high capacity, good cycling stability and reversible transport of aluminium carrier ions (i.e. AlCl₄⁻, AlCl₂⁺ or AlCl₂(urea)₂⁺) have been the most imminent challenges that hinder AIBs from practical applications. In this talk, I will introduce our recent research progress on the design of new cathode materials for AIBs [1-5].

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Boron-doped Diamond Powder for Electrolytic Electrode Material

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Boron-doped diamond (BDD) electrodes are expected to be used as an electrode material for electrolytic water treatment because of efficient generation of OH radical during water decomposition and excellent durability. Conventional BDD electrodes are obtained by deposition of a polycrystalline BDD thin film on a conductive substrate such as conductive silicon wafer or niobium plate via chemical vapor deposition (CVD). Therefore, the BDD electrodes are basically a planar electrode, and are difficult to be obtained as a large-area electrode at low cost. We have developed BDD powder as a conductive diamond powder material, which is expected to be used for various electrochemical applications such as screen-printed electrodes, PEFC cathode catalyst support and electric double-layer capacitors. In this study, in order to apply the BDDP to an electrode material for electrolytic processes, BDDP-packed electrolytic flow cells and spray-coated BDDP/silica electrodes were developed.

BDDP was obtained by deposition of a BDD layer on the surface of insulating diamond powder substrate via CVD. A BDDP-packed electrolytic flow cell was fabricated by filling a cylinder equipped with a glass filter on the bottom with BDDP. Since the BDDPs in the packed bed are electrically connected each other by the contact between the particles, the whole packed-bed can act as an anode. In addition, OH radical generation was confirmed when a voltage of 5 V was applied between the BDDP-packed bed anode and platinum counter electrode in an aqueous electrolyte solution. When electrolysis was performed with a BDDP-packed electrolytic flow cell using methylene blue (MB) as a model organic pollutant, the MB decomposition rate was found to increase according to the amount of BDDP. Moreover, since the electrolytic performance basically did not change even after repeated experiments, the BDDP-packed electrolytic flow cell is expected to be applied to a highly efficient and durable electrolytic flow system for water treatment.

In addition, spray-coated BDDP/silica electrodes were developed toward application to a large-area diamond electrode that can be produced at low cost. A silica sol slurry containing BDDP was spray-coated on a titanium substrate, followed by heating to form a BDDP/silica composite film. When constant current electrolysis of concentrated sulfuric acid was performed for 90 min at the BDDP/silica anode, the electrode potential was stable at a high potential (ca. +3 V vs. Ag/AgCl), showing sufficient durability of the electrode. The sulfuric acid after electrolysis was found to contain active oxidizing species such as peroxodisulfate. Therefore, the BDDP/silica electrode fabricated via spray coating is expected to be used for sulfuric acid electrolysis process.

Gas Phase Photocatalytic CO₂ Reduction and H₂ Production over Anodized Nanotube Arrays

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Electrochemical anodization has been widely employed for fabricating nanostructures of widegap metal oxide semiconductor materials. Anodized metal oxide nanotubes possess self-aligned structures with large specific surface area, which are promising for various practical applications toward electrodes in batteries, photovoltaics, gas sensors, photocatalytic reactors, and so on. In particular, anodized metal oxides prepared with electrolytes including both fluoride and polyols showed a variety of well-controlled nanostructures, and realized high-performance water photooxidation and photocatalytic air purification. Hence, materials research on metal oxide nanostructures play an important role in terms of cost effectiveness and sustainability. In the past several years, I have performed research on photocatalysis and electrical properties of anodized metal oxide nanotube arrays such as TiO₂ and hematite (α -Fe₂O₃). In this presentation, our recent results on photocatalytic carbon dioxide (CO₂) reduction and hydrogen (H₂) production in gas phase over anodized nanotube arrays will be introduced.

So far, a large number of evaluations for photocatalysis based on liquid-phase reactions have been carried out, where gas analysis during photocatalysis mainly detects only final products. On the other hand, evaluation of photocatalytic reactions in high vacuum has an advantage that intermediate products can be observed at a real-time scale. In our group, real-time observation of gas phase reaction processes over nanostructured photocatalytic thin films in high vacuum have been performed by utilizing a home-made apparatus. Here, photocatalytic CO₂ reduction methanol decomposition over Cu₂O-loaded TiO₂ nanotube array (CNP/TNA) and Pt-loaded TNA (Pt/TNA) were examined under ultraviolet-visible (UV-VIS) irradiation (300–600 nm) [1]. The real-time monitored partial pressure changes in various gas species indicated that CO₂ photoreduction arises through hydrogenation reaction in gas phase over CNP/TNA even in high vacuum, although CO₂ deoxygenation reaction is conventionally dominant for gas phase reactions as observed for Pt/TNA [1].

In addition, hydrogen production from gas phase photocatalytic decomposition of water/methanol mixture under visible light irradiation has been verified over TNA decorated with graphitic carbon nitride (g-C₃N₄) nanoparticles (g-C₃N₄/TNA) [2] and Cu₂O-loaded hematite nanotube array (CNP/FNA) [3], while hydrogen production was not observed with only TNA and FNA. The direct Z-scheme mechanism can be partially contained in the charge transfer process at the CNP/FNA interfaces as well as at the g-C₃N₄/TNA interfaces. A series of the experimental results suggests that nanoparticles of Cu₂O and g-C₃N₄ are effective as noble-metal-free co-catalysts for visible light responsive photocatalysis based on vertically aligned nanotube arrays.

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Band Structure of Ferrites Doped Gd_2O_3

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We report experimental measurement of the fundamental absorption edge in nickel zinc ferrite doped Gd_2O_3 . Doping was done through thermal decomposition of the mixture at 1000°C . The average grain size of the thermally decomposed mixture was determined to be around 95 nm and contained phases of cubic Gd_2O_3 , GdO , and orthorhombic prisms of GdFeO_3 . The imaginary part of the complex dielectric function was calculated from the absorbance measurements that showed an optical band gap at 1.8 eV. The observed value of the fundamental energy gap is on average 4.0 eV smaller than suggested by early experiments. A model for the ferrite doped Gd_2O_3 was constructed to suggest that the Ni, Zn, and Fe atoms occupy Gd sites in the Gd_2O_3 lattice. A new band at Γ point is formed due to the hybridization of the atomic orbitals of dopant and Gd^{3+} that shifts the fundamental absorption edge to the red part of the photon energy spectrum. Despite having a high density of negatively charged carriers contributed by the dopant, the onset of the direct interband transitions is clearly resolved.

Optical and Electrical Properties of Photovoltaic Materials via Luminescence

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In nature, many materials have their unique light emission fingerprints. These fingerprints are strongly dependent on material properties, device structures, surrounding environments, and measurement conditions. These complex relationships provide us with unique opportunities to explore the properties of photovoltaic materials and devices by performing light absorption and emission measurements from above the sample surfaces. A photovoltaic device can emit many luminescence peaks under appropriate excitation conditions. By investigating the fundamental properties of these peaks (energy, shape, and intensity) and their evolutions versus various fabrication and measurement conditions, we can extract many critical properties of the device. This talk will present the physics and our recent advances in luminescence spectroscopy and imaging techniques to characterise photovoltaic materials and devices, including silicon, perovskites, and two-dimensional materials. Many of these techniques could be applied to other energy materials.

Conversion of Carbon Dioxide to Useful Substances by In-liquid Microwave Plasma CVD

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1.Introduction

In recent years, highly efficient CO₂ reduction technology is needed. Here, we focused on a new technique, in-liquid microwave plasma CVD. In this method, microwaves are introduced through electrodes to decompose solvents in bubbles and generate plasma. This method generates high-temperature, high-energy plasma at a high density in the bubble, enabling high-speed reactions to occur. In addition, since the solvent acts as a proton and electron source for the reaction, more complex compounds can be generated compared with conventional atmospheric pressure plasmas. Furthermore, it is known that this technique can decompose alcohol and produce diamond [Terashima, Diamond and Related Materials (2016)]. Since methanol can be decomposed to C, CO₂ reduction by this method can be expected. This study aims to convert CO₂ to useful substances by the microwave in liquid plasma method.

2.Experimental

The reactor was filled with 400 mL solvents of water or methanol. CO₂ gas was introduced directly into the plasma from the outside using a hollow electrode. The metal substrate as a counter electrode was attached to the substrate holder. While the microwave output was fixed at 450 W, the pressure inside the reactor and the distance between the substrate and electrode were changed to study under several conditions. The plasma emission spectrum was measured. The generated gasses inside the reactor during the plasma treatment were evaluated by gas chromatography and in-situ FT-IR Spectroscopy. Liquid products in water were evaluated by ion chromatography.

3.Results and Discussion

First, plasma generation in water was conducted at pressure inside the reactor of 20 kPa and distance between the substrate and the electrode of 3 mm (condition (1)). Similar experiments were conducted under the conditions of 20 kPa and 5 mm (condition (2)) and 10 kPa and 3 mm (condition (3)). Gas chromatography confirmed that CO was formed after plasma treatment at all conditions. CO concentration measured by in-situ FT-IR during plasma generation showed that the plasma treatment under condition (1) brought the highest CO generation. The conversion rate to CO is 4.47%. Because the emission spectrum from plasma generated only under condition (1) showed high intensity in the infrared region, the plasma generated under condition (1) had the highest temperature. Higher temperature of the plasma facilitated the dissociation of the C=O bond of CO₂, leading to CO production. Plasma generation was also conducted in methanol under similar conditions, however the conversion did not improve. In addition, ion chromatography was applied to examine liquid products in the water after the plasma generation, and formic acid and acetic acid were detected.

4.Conclusion

We succeeded in CO₂ reduction by introducing CO₂ directly into the plasma and reduced products such as CO, formic acid, and acetic acid were confirmed. The highest reduction rate was achieved under the conditions (1), in which a reactor pressure and a substrate-electrode distance was 20

kPa and 3 mm, respectively. Although reduction efficiency is still low, further improvement of the reduction rate can be expected by optimizing the solvent, pressure, catalyst, and other factors.

Composite Structural Supercapacitor Design with Carbon Nanotubes Electrodes, Boron Nitride Nanotube Separator and Localised Ionic Liquid Electrolyte

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The increasing demands for energy storage require constant research and materials development. There is a lack of technology particularly for applications that require both high energy density and power density. Supercapacitors have shown promise as they far exceed the sustained power performance of battery technology with far less weight and volume requirements than electrolytic capacitors. Automotive and aerospace vehicles have high power requirements and come with additional design requirements towards improving weight and volume savings. Incorporation of supercapacitor technology into the structures in these vehicles is one approach being explored in the literature. Fibre reinforced composite structures are particularly advantageous due to their layered structures, where supercapacitors can be incorporated between multiple layers of the composite. If inherently structural materials are used as electrodes and separators, these devices can be integrated into composites and bare load, becoming structural supercapacitors (SSC).

The developments of composite SSCs at DSTG are fabricated with carbon nanotube electrodes, glass fibre separators and localised ionic liquid electrolytes, [1] these show promising electrochemical performance and minimal impact on the bulk composite structure. [2] The specific energy of the electrodes has been improved by oxygen functionalisation of the CNTs by ozonolysis, providing additional pseudocapacitance. The power performance of these SSCs can further be improved by using thinner structural separator materials such as boron nitride nanotubes (BNNTs), reducing the spacing between the electrodes, while maintaining robust separation of the electrodes. DSTG has initially achieved this through deposition of the BNNTs directly onto the glass fibre separator layer to enable thinner and more open weave glass fabrics to be employed. [3]

Here we shown the designs, methods and morphology of manufactured composite SSC flat panels that are suitable for integration into structural components used in transport industries. These composite SSCs typically include ozone functionalised CNT electrodes, thin directly deposited BNNT separators and localised ionic liquid electrolytes, cured within high-performance aerospace composites. The electrochemical performance of these SSC panels and structures will be detailed, including cycling stability, energy and power performance and compared to the relative mechanical performance.

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Development of High Water-resistant Photocatalytic Coating on Plastic by Using a Surface Modified TiO_2 with Silane Coupling Agents

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1. Introduction

Drinking water in developing countries is polluted with bacteria such as *E. coli* and *Salmonella*, therefore, a water treatment technology is highly needed. We focused on titanium dioxide (TiO_2), which is an inexpensive photocatalyst. It can destroy bacteria by constantly oxidizing them after they destroy their cell membranes due to the powerful oxidizing power of reactive oxygen species, which are formed under UV light irradiation. Nevertheless, large mass treatment, easy to use, inexpensive water treatment technology has not been reported. Therefore, we aimed to create a TiO_2 supported net that can easily purify water. Photocatalytic activity of the created net in the first trial was confirmed by the decomposition of methylene blue. However, the photocatalyst layer on the surface peeled off after 3 days of net floating on water under the sunlight, thus we improve the adhesion stability by using plasma treatment and silane coupling agent modified TiO_2 .

2. Experimental

Silane coupling agents (3-aminopropyltriethoxysilane (APTES) or Hexyltrimethoxysilane (HTDMS)) was hydrolysis in deionized water, EtOH and formic acid. Then, the TiO_2 were added. The mixture was kept refluxing for 5 h. After that, dispersed particles were washed with ethanol. Modified particles were dried in an oven. TiO_2 supported net is fabricated by the successive coating on a polypropylene net. First, silicone resin (methyl phenyl polysiloxane) as a protective layer was coated by dip coating. Second, silicone layer coated net was treated with O_2 plasma by using parallel plate reactive ion etching system to improve the surface wettability. Third, modified TiO_2 powder (P25) and a silicone resin were mixed and coated on the silicone resin protective layer. After coating processes, the net was placed in an oven and dried for 20 min at 100°C . Water-resistance of the coated layer was investigated from SEM images after floating the photocatalyst net in water under sunlight. The photocatalytic property change through outdoor exposure was checked by the decomposition of methylene blue.

3. Results and Discussion

The silicone protective layer and HTDMS modified TiO_2 only maintained surface TiO_2 coating after

49 days of net floating on water under the sunlight. (non-modified TiO_2 and APTES modified did not.) By using methyl phenyl polysiloxane for silicone layer, the high hydrophobicity of phenyl group caused high water-resistant. Plasma treatment increased -OH group and improve the wettability of the silicone layer. Therefore, a stronger adhesion between the layers was obtain. Also, it showed a higher photocatalytic property in decomposition of methylene blue. This is because the layers contain more TiO_2 particles due to the wettability. It can be considered that HTDMS modified TiO_2 showed a great water resistance due to its long carbon chain. This carbon chain tangles in the silicone chain and physically improve the adhesion.

4. Conclusion

We obtain TiO_2 modified with APTES and HTDMS by using a silane coupling agent. By modifying the surface of TiO_2 particles and treating the surface of the silicone layer by plasma, we succeeded in high water-resistant photocatalyst coating that can be coated at low heat and maintained for 49 days.

Oxidation of Silver Nanoparticles at High Temperatures by Reactive Molecular Dynamics

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Silver nanoparticles (nanosilver) is one of the most extensively studied nanomaterials due to its multiple applications in catalysis and biomedicine (Pulit-Prociak et al., 2015). The oxidation of nanosilver is closely related to its antibacterial and optical activities, therefore, its properties could be modified if the oxidation degree is controlled. However, the reactivity of silver nanoparticle in the presence of oxygen has not been quantified, and studies of the oxidation rate of nanoparticles, especially in the sub-10 nm scale, are scarce. Here, reactive molecular dynamics (MD) are used to simulate the oxidation of silver nanoparticles of different diameters at high temperatures like those in flame pyrolysis synthesis (Sotiriou et al. 2012). The simulations are validated by the size-dependent melting point of nanosilver, which is in excellent agreement with non-reactive MD simulations (Zhao et al. 2001; Xiao et al. 2005; Buesser et al. 2015) and experiments (Tang et al. 2008, Castro et al. 1990). The formation of a silver oxide on the nanoparticle surface is investigated by tracking the number of Ag and O atoms as function of the distance from the center of mass of silver nanoparticle during oxidation at temperatures higher than 600 K, consistent with temperature measurements in flames. The nanoparticle core is composed only by Ag atoms, while in the nanoparticle surface an oxide layer is formed, indicating that oxidation occurs externally. Oxidation also leads to a complete loss of the nanoparticle crystallinity due to the atomic motion induced by the silver oxide layer. The oxidation rate of nanosilver is estimated by using the shrinking core model, for the first time to our knowledge, from the MD simulations. Faster oxidation is observed for small particles and high temperatures, consistent with experiments of Al nanoparticles (Park et al. 2005).

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Design of 2D Ferroelectric Heterogeneous Catalysts for Controllable Hydrogen Evolution Reaction

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Understanding the decisive factors of electrochemical reactions and developing the effective manipulation strategies are crucial for the rational design of highly active catalysts and renewable energy conversion technologies. In this work, with transition metal embedded in nitrogen-doped graphene (TMN₃) as the example, it is found that the electron doping and band shift are the dominant factors for HER activity by using first principle calculations, indicating the possibilities to design the optimal catalysts by the manipulations of charge densities and band states near the Fermi level. Here, a novel approach to achieve hydrogen evolution reaction (HER) control via ferroelectric (FE) switching is proposed. Our theoretical results reveal that the electrocatalytic HER performance of TMN₃ catalysts can be well controlled when it is placed on the surface of FE In₂Se₃, in which CoN₃/P↓-In₂Se₃ exhibits the best HER performance with the Gibbs free energy change of -0.044 eV. The adsorption energies and charge transfer can be effectively modulated when the polarization is reversed, due to the polarization induced electron redistribution, spin moment changes, and band state shifts near the Fermi level. The FE-controlled HER activity is further supported by the catalyst-electronic-magnetic relationship under the electric field. This systematic study provides a fundamental understanding for new insights into the design and application of cost-effective 2D ferroelectric heterostructure catalysts.

Deep Eutectic Solvents for Rice Husk Treatment for Sustainable Battery Material

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Global demand for rechargeable Li-ion batteries has risen steeply due to their versatile potential and has ultimately increased the extraction of minerals. Battery components such as cathode and anode materials are mainly extracted by the mining process and have their limitation such as restricted geographical availability, impact environment as it releases toxic greenhouse gases, and non-sustainable resources, hence an alternative source for the battery material is necessary¹. The use of alternative energy sources such as biomass has become a major focus for the energy storage market as a renewable source due to its carbon neutrality and abundance on the planet². In terms of silicon-based anode materials for rechargeable batteries, silica-rich rice husk is an abundant and sustainable agricultural waste, which can be an attractive alternative to producing silicon/carbon (Si@C) materials³. Several million tons of rice husk wastes are generated in Australia each year, where it is either (a) left in the field, (b) disposed of directly in landfill, or (c) used as low-value agricultural items, such as fertilizer additives, stockbreeding rugs, and bed soil⁴. Hence, utilizing such waste biomass as a precursor for silicon/carbon preparation will reduce Australia's carbon footprint and have definite potential for Australian primary producers to value-add and sell into the future high-growth batteries anode market. This research aims to develop sustainable, low-cost rice-husk-derived silicon/carbon composite anodes using scalable techniques for next-generation batteries. The objectives will be achieved by exploring novel green pre-treatment and processing methods and modifying electrodes and electrolytes. The outcomes will provide an alternative biomass market and help address energy security and climate change issues that currently challenge the global community.

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3D Printed Graphene Aerogels for Energy Storage and Conversion

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Despite significant efforts on graphene-based electrocatalysts for fuel cell applications, it remains a major challenge to fabricate 3D-structured graphene with high conductivity and tailored hierarchical porosity for catalyzing the reactions at the electrochemical interfaces. Conventional fuel cells are heavily dependent on platinum-based electrocatalysts to accelerate the electrochemical reactions, making them too costly and unsustainable for widespread applications. Graphene is an emerging novel two-dimensional material with a large surface area and high electrical conductivity, allowing to use them as a catalyst or catalyst support. One

of the main drawbacks of the utilization of graphene is that they tend to restack due to the strong π -stacking interactions between sheets, leading to a decrease in the availability of active sites. Therefore, three-dimensional graphene-based aerogels have attracted significant interest in clean energy applications due to their high conductivity, extremely low bulk density, high specific surface area, and excellent mechanical strength. Traditional methods for the creation of 3D porous graphene (e.g., self-assembly, sacrificial templates, coating on metallic foams, and crosslinking) are facing significant limitations, such as low scalability, high-cost, complex processes, and poor controllability over the architectures and designs. Therefore, research has driven toward 3D printing for the layer-by-layer fabrication of 2D graphene sheets into functional 3D structures. Unlike conventional methods, 3D printing offers excellent capabilities to fabricate 3D graphene aerogels in a programmable, versatile, and rapid manner. However, state-of-the-art techniques for 3D printing of graphene aerogels often employ excessive non-conductive additives (e.g., surfactants, dispersants, plasticizers, and binders) to retain its 3D porous structure, which is problematic. The presence of these additives is inevitable and detrimental to the final electrical properties of the graphene-based electrodes. Therefore, the construction of electroactive 3D printable graphene aerogels without non-conductive additives is sought after, especially for green energy applications. Here, we report the development of extrusion 3D printable graphene inks by interfacing graphene with recrystallized nanofibrillar conducting polymers. The formulated inks exhibit excellent rheological properties, which can be 3D printed into multilayer (up to 30 layers) structures via direct ink writing (DIW). The formulated inks were used for fabricating 3D printed electrodes for supercapacitor and electrocatalyst layers for oxygen reduction reaction in fuel cells, with excellent performance and stability.

Thin Diamond Films as a Functional Material for Gas-Sensing, Electrochemical, and Energy Conversion Applications

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Advances in the synthesis of diamond in the form of polycrystalline coatings have contributed to a rapid development of several important applications, where synthetic diamond coatings are integrated as functional components. Outstanding resistance to corrosion, chemical inertness, electrical conductivity tunable by control of doping, and high optical transparency characteristics of diamond coatings have driven the implementation of polycrystalline diamond in electrochemical wastewater treatment, ozone generation, photovoltaics, supercapacitors and various sensor applications [1]. Although polycrystalline boron-doped diamond (BDD) have been acknowledged as a material exhibiting properties superior to those offered by conventional electrode materials, implementation of diamond in real-world applications has lagged behind alternative materials, which offer a greater degree of versatility. For commercialization of diamond for relevant applications, the readiness of the diamond synthesis technology along with approaches on fabrication of diamond coatings in various forms (i.e. planar or structured) in a practical and scalable manner are required today.

In this work we present steps towards development of nanocrystalline BDD layers as the platform for fabrication of gas-sensor system for the detection of harmful gases. To achieve higher sensitivity, selectivity and stability towards detection, we first concentrate on the selection of important BDD electrodes synthesis characteristics, such as the concentration of boron dopants and process gas chemistry. We demonstrate synthesis of BDD coatings at different temperatures to allow for the implementation of temperature-sensitive substrate materials, such as those used in flexible-type gas-sensors. Additionally, we demonstrate that nanocrystalline BDD layers can be fabricated on a large area (wafer-compatible) [2], implemented as electrochemical electrodes for water treatment [3], and optically transparent/electrically conductive coatings for energy-conversion devices [4,5]. Finally, we present feasibility of fabrication of nano-structured (porous) BDD electrodes, which can deliver significantly higher levels of functionality and efficiency to gas-sensing and electrochemical applications.

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Molybdenum-promoted Surface Reconstruction in Polymorphic Cobalt for Initiating Rapid Oxygen Evolution

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It is well known that the surface reconstruction of electrocatalysts in the form of phase transition, defect migration, and valence adjustment at the initial stage plays a crucial role in generating truly surface-active catalytic centers and achieving stable surface reactions. A low activation energy barrier for initiating surface reconstruction is also expected to be crucial for fast and stable electrochemical catalysis. Despite this, the kinetics of surface reconstruction and its impact on catalytic reactions have been rarely studied. Here, real-time X-ray photoelectron spectroscopy (XPS) structural monitoring of surface chemical state evolution during catalytic reactions is performed using a phase-modulated polymorphic Co-based catalyst with customizable nitrogen-metal bonds via a cationic molybdenum substitution strategy to track Kinetics of initial surface reconstruction during the alkaline oxygen evolution reaction (OER). It is concluded that molybdenum-modulated cobalt-based nanocatalysts can be tuned through good initial surface reconstruction and stable active centers to achieve optimized OER catalysis, accompanied by a low onset overpotential of only 210 mV and 10 mA cm⁻² has a favorable overpotential of 290 mV, which is better than that of commercial noble metal RuO₂ catalysts. Thus, this study provides new conceptual insights into the rational tuning of the initial surface remodeling kinetics for high-performance electrocatalytic reactions.

Biom mineralization Inspired Dendrite-free Zn-electrode for Long-term Stable Aqueous Zn-ion Battery

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Rechargeable aqueous Zn-ion batteries (AZIB) are a promising type of energy storage device, but suffer from the growth of uncontrollable Zn dendrites, which result in the shortcut of the battery. Herein, inspired by the regulated nucleation and growth of inorganic minerals from porous organic matrix within the biom mineralization process, dopamine derived N-doped carbon spheres with abundant gaps and voids are assembled onto the Zn metal anode (Zn@C) as an artificial solid electrolyte interphase (SEI) layer to modulate the nucleation and growth of a smooth Zn layer without dendrites and suppress the corrosion and hydrogen evolution side reactions. When assembled into Zn-ion batteries, the bioinspired electrode presents comprehensive enhancements in terms of capacity, rate performance, and stability. This unique design of electrode allows long-term stable cycling up to 2,100 h at 5 mA cm⁻² for a symmetric battery and gives rise to the performance of 315 mAh g⁻¹ at 0.5 A g⁻² and 95% retention of its original capacity after 1,000 cycles for the Zn@C//V₂O₅ pouch cell, which outperform most of reported Zn electrodes. The flexible pouch cells displace significant durability towards folding, bending, and piercing, demonstrating its capability for practical applications in wearable devices.

Session: Advanced Characterizations and Computational Materials

Application of Advanced Mineral Analysis and Characterization System (AMICS) in Material Research

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AMICS consists of a (i) Hitachi scanning electron microscope (SEM), (ii) Bruker energy dispersive spectroscopy detector (EDS), and (iii) the original software that takes control of both the SEM and EDS, collects the data, processes EDS and mineral maps, and generates images, graphs, and tables ready for reporting and publications. Traditionally, the system would acquire an EDS map, analyze multiple EDS spectra (for each pixel of a back scatter electron image), compare them to these from a mineral database, and generate a mineral map of the sample. Each mineral in the sample map would be match to a “standard” chemical composition stored in the database. Currently,

the major areas of application for this system are geology, mining, mineral processing, and ore enrichment. Assuming that natural minerals are multi-phase ceramics, the principles of chemical analysis utilized in AMICS could be extended to characterization of a broad spectrum of multi-phase man-made materials, such as metal alloys, composites, and powders. This presentation will outline the system capabilities and showcase the characterization results obtained on a number of materials: rocks, steel, nano-particles.

Experimental Measurements of Chemical-bonding Structure Factors in Nanostructured Materials

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Chemical bonding is the basis of almost all materials properties and many theoretical models of bonding, such as density functional theory (DFT) for example, are used (often blindly) to predict the properties of materials that are designed for specific applications. While such theoretical methods are ubiquitous in materials science, experimental methods are far less prominent because of the limited types of materials that can, at present, be probed with them. The accurate and high-resolution mapping of chemical bonding structure in three dimensions has been entirely confined to single-phased homogeneous materials for many physical reasons that we will not go into the details of in this abstract.

The present work applies a recent adaptation to quantitative convergent-beam electron diffraction (QCBED) — known to be the most accurate and precise experimental technique for measuring chemical bonding structure — that permits the measurement of bonding-sensitive structure factors around a nanostructure in a crystalline host material for the first time.

The significance of such an advance is not to be underestimated considering that most materials in service are not homogeneous and single-phased but are likely to contain a myriad of nanostructures. The inhomogeneities tailor the properties of the materials in which they are intentionally grown, through hybridisation with the properties of the host matrix. Understanding the function of nanostructures in host matrices and the functional relationships between the phases in a nanostructured material at their most fundamental level, necessitates an understanding of chemical bonding structure in all of the constituents. Measuring and mapping chemical bonds in and around nanostructures and their host material, both in situ and as a function of position with respect to each of the different phases, is central to gaining such an understanding.

Molecular Modeling of Anti-fouling Properties of Polymer Membrane Surface

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In water treatment polymer membranes, the phenomenon of protein or organic matter adhesion is known as fouling, and it causes significant water flux reduction. Therefore, it is necessary to develop membrane resistant to fouling in order to maintain stable water permeation. There are various theories on the mechanism of fouling, but it has been reported that the intermediate water between the foulant and the polymer membrane surface plays an important role. In adhesion phenomena at polymer surfaces in an aqueous solution, there is a weak interaction between polymer materials and organic materials such as proteins, which always act as an attractive force in a vacuum. However, in water, hydrophobic and hydrophilic interactions develop due to the entropic effect of water molecules, and the interaction between the protein and the polymer surface changes significantly. We used molecular dynamics (MD) to quantify intermediate water affected by various polymer membranes. In this presentation, to understand the fouling behavior of proteins on polymer membranes, we will present the results of simulations of the behavior of water presented between surfaces of self-assembled monolayers when they are brought close to each other and the behavior of intermediate water at the interface when proteins approach the membrane surface.

Towards *In-situ* Observation of Potassium Electroplating and Stripping Processes in a Transmission Electron Microscope

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Research attempts on discovering efficient rechargeable battery alternatives for the widely used lithium-ion batteries have been growing in the past decade as it is known that lithium resources are limited as well as unevenly distributed in the earth's crust. The newly developed potassium-ion batteries [1] are considered to have a great potential to replace or complement lithium-ion batteries since more abundant resources of potassium are available. Low fabrication costs, faster charging and a higher operating voltage may be expected in these batteries. Similar to the case with lithium-ion batteries, a variation of potassium-based batteries with a metal negative electrode may be attractive, removing the need for a dedicated intercalation electrode material and promising a higher energy density [2].

Although many phenomena may be investigated using conventional ex-situ analyses, advanced in-situ techniques are preferable and enable us to observe and measure parameters in real-time processes, opening up the possibility of revealing unexpected results. Currently, we are progressing towards observing the electroplating and stripping processes of potassium through in-situ transmission electron microscopy. The experimental setup [3] for this in-situ TEM observation allows us to carry out charge and discharge cycles in a system where the electrodes are immersed in a liquid electrolyte, which simulates an operating battery at a smaller scale. This presentation will describe our experimental steps undertaken towards the in-situ observation of potassium plating and stripping, starting from preliminary test experiments in an aqueous electrolyte and continuing to more complex experiments in organic electrolytes with lithium and potassium salts.

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Investigation of CO₂ Permeation Mechanism on Mixed Matrix Membrane Using Non-molecular Dynamics Simulation

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Mixed matrix membranes (MMMs), which consist of inorganic porous particles (filler) dispersed in a polymer (matrix), have attracted attention as a membrane that exceeds the performance of conventional polymeric membranes. The gas permeation on MMMs depends not only on the interaction between the MMMs and the gas but also on the affinity between the matrix and the filler. Especially, the effect of voids between the matrix and filler is very important for membrane performance. In this study, a non-equilibrium molecular dynamics (NEMD) simulation was performed to investigate the CO₂/CH₄ mixed gas permeation in MMMs containing MFI-type zeolite particles mixed with the polymer of intrinsic microporosity-1 (PIM-1), a type of microporous polymer. And, the pathways of gas permeation and structural changes of the membrane were analyzed at the molecular level.

The NEMD method can model and simulate arbitrary membrane structures. In the NEMD method, the number of molecules is controlled in each region by setting up a generation layer and a deletion layer of gas molecules through the membrane model in the calculation cell. This creates a difference in the collision frequency of gas molecules against the membrane upstream (Feed) and downstream (Permeate) of the membrane model, thus enabling the simulation of steady-state membrane permeation phenomena driven by pressure differences. Molecules that are reflected from the surface of the membrane and return to the emergent layer are removed as they are not involved in the membrane permeation. On the other hand, molecules that permeate the membrane and reach the bottom of the membrane are eliminated in the removal layer. This process is repeated until the number of gas molecules in the membrane reaches a steady state. The flux is calculated by counting the number of molecules that have permeated the membrane. The MMMs model in the NEMD simulation was created by packing 22 pentameric PIM-1 monomers and one MFI zeolite particle. The interaction parameters between PIM-1 and gas molecules and between MFI zeolite and gas molecules were optimized by fitting the adsorption isotherms calculated using the grand canonical monte carlo (GCMC) simulations to the experimental data.

The NEMD results showed that PIM-1 swells by the sorption of CO₂ molecules. And, these results indicated that the NEMD model of a fully swollen PIM-1 membrane is not CO₂-selective. In contrast, the CO₂ selectivity on the MMMs model was approximately double that of the PIM-1 model. The value of volume change in the NEMD model of MMMs was smaller than that of the PIM-1 model. These results indicated that the addition of MFI particles suppresses the swelling of the PIM-1 phase. Furthermore, the permeation pathways of CO₂ molecules were analyzed by classifying them into three pathways: the zeolite phase, the interface between PIM-1 and zeolite, and the PIM-1 phase, and it was found that the highest number of CO₂ molecules permeated the zeolite phase, followed by the interface, which was the most selective. At the conference, we will discuss the gas permeability and void effects from the results of permeation pathways.

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