



PRISM

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# Materials Science and Engineering



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## ABSTRACTS



**Day 0:** Sakata-Hirata Hall  
Nagoya University, Japan

**Day 1-3:** Noyori Conference Hall  
Nagoya University, Japan

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## Session: JST-ERATO Special Session

**Bio-Nano Science – Insights for Nanomedicine****Frank Caruso***Department of Chemical Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia*

Self-assembly technologies have been used extensively to engineer a diverse array of particles for biological applications, including therapeutic delivery. This presentation will focus on our research on the development of particles and their interactions with biological barriers. Aspects of the physicochemical properties of the particles, post-assembly biological modification, ligand targeting, and the formation of protein coronas will be covered. Particle variants based on metal–ligand complexation will also be highlighted. Our studies are aimed at obtaining detailed knowledge of complex bio–nano interactions to aid in the rational design of nanoengineered materials for applications including HIV, hearing loss, and cancer targeting.

**Micro Elastofluidics: Elasticity and Flexibility for Efficient Microscale Liquid Handling****Nam-Trung Nguyen,<sup>a\*</sup>***<sup>a</sup>Queensland Micro- and Nanotechnology Centre, Griffith University, 170 Kessels Road, Nathan, Queensland 4111, Australia*

Although progress has been made in materials development and flexible electronics, microfluidics in wearable and implantable systems remains an almost unexplored area. There are practical and fundamental reasons for the slow progress in this area: (i) current lab-on-a-chip and organ-on-a-chip devices require bulky lab equipment such as syringe pumps and microscopes to operate, and are not practical for wearable devices; (ii) most wearable systems are continuous-measurement tools that require a different design approach than conventional single-measurement lab-on-a-chip devices; (iii) storage of samples in vials and syringes, as well as their continuous delivery using pumps, makes them too bulky and not practical for wearable systems; (iv) the flexible and conformal nature of wearable/implantable systems does not allow for the implementation of established methods in conventional rigid microfluidics [1]; and most importantly, (v) the fundamentals of fluid–structure interactions, and the effect of structural flexibility and elasticity on storage, mixing, separation and delivery of liquids in molecular scale and macroscale, are not understood well enough to enable suitable engineering solutions. This talk presents our recent promising results in the field of micro elastofluidics, utilising flexibility and elasticity from molecular scale to device scale. Typical examples are enhanced mixing and separation with viscoelastic fluids, liquid storage and handling with liquid beads and tuneable microfluidic devices for separation and handling of biological particles.

**Carbon-based Materials for Catalytic Oxidation****Shaobin Wang***<sup>a</sup>School of Chemical Engineering, The University of Adelaide, SA 5005, Australia*

Currently, we are facing several global issues in energy shortage and environmental pollution and need novel technologies to tackle with the various problems. Nanomaterials and nanotechnology are important in different industrial processes for chemical synthesis, energy conversion and environmental remediation. Metal-free carbocatalysts, featuring low costs, environmental friendliness, long-term durability, tunable

structure and facile regulation of surface chemistry, have been widely exploited in heterogeneous catalytic reactions and exhibit remarkable activities.

In the past ten years, we have been focusing on developing nanocarbon-based materials for catalytic organic oxidation in water/wastewater treatment. Compared to metal- or metal oxide-based catalysts, carbon materials can avoid secondary contamination due to toxic ion-leaching and toxicity. A new Fenton-like system based on persulfate/carbon has been developed and demonstrated high efficiency in oxidative degradation of different types of water contaminants and water disinfection. We found that the carbocatalysts can effectively activate persulfates to produce versatile highly reactive oxygen species including radicals ( $\text{SO}_4^{\bullet-}$ ,  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$ ) and nonradical species (electron-transfer pathway and  $^1\text{O}_2$ ) for oxidizing and mineralizing a wide array of aqueous organic pollutants. In addition, carbon/persulfate systems were also found to be effective for chemical synthesis. Deliberate material design and density functional theory (DFT) calculations were integrated to unveil the intrinsic active centers of carbon materials in persulfate activation as well as the structure-performance relationships in carbocatalysis. Meanwhile, the role of edges, topological defects, oxygen functionalities, carbon dimensions, hybridization ( $\text{sp}^2$ ,  $\text{sp}^2/\text{sp}^3$  or  $\text{sp}^3$ ), and hybrid effect were systematically investigated and the origins of radical and nonradical pathways were also elucidated.

## Photochemical Action Plots Reveal the Fundamental Mismatch between Absorptivity and Photochemical Reactivity

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Over the last decade, our laboratory has employed monochromatic tunable laser systems to reveal a fundamental mismatch between the absorptivity of a chromophore and its photochemical reactivity in the vast majority of covalent bond forming reaction as well as specific bond cleavage reactions. Our data overturns the long-held paradigm that effective photochemical reactions are obtained in situations where there is strong overlap between the absorption spectrum and the emission wavelength. However – as we explore herein – the absorption spectrum of a molecule provides only information about singlet excitation and remains entirely silent on the accessibility of the critical triplet states, which dictate photochemical reactivity. We propose future avenues of enquiry on how action plots can be understood and explore how they are of key importance for tailoring photochemical applications in soft matter materials design with never-before-seen precision.

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## Theoretical and Computational Molecular Science: Nonequilibrium Systems, Fluids and Materials

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Theoretical and computational molecular science is now a technique that is widely applied in materials science. It is used to provide predictions on the performance of new materials and processes, to test hypotheses made based on other techniques and to explore material behaviour at time and size scales that are inaccessible using other techniques. It enables a deep understanding of the physical and chemical mechanisms involved and does this without disturbing the system. However, new methodologies are continually being developed that allow computation to model more complex systems undergoing more complex behaviour.

Much of our recent work has been motivated by the need for better energy storage systems and also for high quality materials for electronics applications. In this talk some recent results will be presented spanning simulation of supercapacitors,<sup>1,2</sup> measurement of diffusivity and conductivity in electrolytes<sup>3</sup> and growth of high-quality 2D materials.<sup>4</sup>

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## Nanomaterial Properties as Revealed by *in situ* Transmission Electron Microscopy

**Dmitri Golberg**

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The knowledge of electrical, mechanical, thermoelectric and optoelectronic properties of nanomaterials is of prime importance as far as their smart integration into modern technologies is concerned. However, typically, such properties have been measured using instruments having no direct access to the material atomic structure, its defects, crystallography and spatially resolved chemistry. This drawback largely limits

the relevance of data because many structural features of a nanomaterial prior, during and after its testing have been hidden. Therefore, the acquired results cannot be linked to a particular material morphology, its atomic structure, and defects' network. This shortcoming has confused engineers and technologists and leads to many uncertainties with respect to realistic nanomaterials' applications and industrial potentials. I will demonstrate the full usefulness of state-of-the-art *in situ* transmission electron microscopy (TEM) techniques for properties/functions analysis of diverse frontier materials, e.g., carbon,<sup>1</sup> boron nitride and dichalcogenide nanotubes and nanosheets, inorganic nanowires, nanoparticles and nanocomposites. Elasticity, plasticity, fracture strength and toughness, electrical resistivity, thermal gradients, photocurrents,<sup>2</sup> photovoltages and spatially resolved luminescence of a nanomaterial may now be unambiguously determined inside TEM, while employing piezo-driven probes, sensors and nanomanipulators and/or optical fibers inserted into the TEM column.<sup>3</sup>

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## Uncovering the Radical Character of Quinone Dimethides

**Michelle L. Coote,<sup>a\*</sup> Zhipeng Pei<sup>a</sup> and Michael S. Sherburn<sup>b</sup>**

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Electrons usually prefer to be paired, and species with even numbers of electrons tend to exist as ground state singlets. Initiation of radical reactions by non-radical species usually requires light, heat or catalysts such as *N*-heterocyclic carbenes. *para*-Quinonedimethide (pQDM), the simplest structural subunit in graphene, is an important and rare exception. While it is a ground state singlet with a large singlet-triplet excitation gap, we have recently provided the first experimental and theoretical proof that its dimerisation occurs via a non-photochemical radical mechanism. We also show that, despite being formally a non-radical, pQDM can be trapped by TEMPO, and can even be used to initiate radical polymerization of acrylates under mild conditions in the dark.<sup>1</sup> Interestingly, tetracyanoquinonedimethide, an important and closely related derivative, does not react in the same way despite having similar radical character. We show that this is due to a combination of polar and steric effects, implying that the diradical reactivity and associated stability of these simple nanographenes can be tuned through simple structural changes.<sup>1</sup> Moreover, the diradical process responsible for pQDM dimerization and polymerization is also responsible for the autoinitiation of (meth) acrylate polymers, albeit at much higher temperatures (> 200°C).<sup>2</sup> However, our unpublished work suggests that, due to the ability of electric fields to stabilize radicals,<sup>3</sup> this reaction can also occur under much milder conditions in the presence of an acid catalyst with applications for initiator free radical polymerization.<sup>4</sup> In this presentation, we will outline these surprising results and discuss their broader fundamental importance for understanding and harnessing diradical reactivity in synthesis, and for understanding the structure-reactivity properties of nanographenes.

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## Session: Biomaterials, Bioengineering and Bio-related Applications

### Chiral Mesostructured Inorganic Materials with Various Chiral Anisotropy

**Shunai Che \***

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Various inorganic materials with multi-chiral hierarchical mesostructures (SiO<sub>2</sub>, TiO<sub>2</sub>,<sup>1</sup> CuO,<sup>2</sup> ZnO,<sup>3</sup> SnO<sub>2</sub>, Carbon, CdSe@CdS,<sup>4</sup> BiOBr,<sup>5</sup> Ag, Cu,<sup>6</sup> Au,<sup>7,8</sup> NiO,<sup>9</sup> Fe<sub>3</sub>O<sub>4</sub>,<sup>10</sup> Fe<sub>2</sub>O<sub>3</sub>, hydroxyapatite), ranging from the atomic to micrometer scale were synthesized by cooperative self-assembly of chiral templates, such as, amino acid derived amphiphiles, DNA and peptides, small chiral molecules, and inorganic sources. These materials exhibited various chiral anisotropy (ChA), such as photo-ChA (i.e. OAs including reflection-, absorption-, and emission-based OAs),<sup>1-10</sup> electrocatalytic-ChA,<sup>6</sup> Surface-Enhanced Raman Scattering-ChA,<sup>7</sup> Photomagnetic-ChA,<sup>8</sup> Resistance-ChA,<sup>9,10</sup> cell regulation-ChA, etc. The multi-OAs with remarkably prominent selectivity are due to the additional selective light-harvesting that occurs the reflection-based OA overlaps with the absorption- and emission-based OA. Recently, it has been discovered that chiral structure Cu has enantioselectivity for various amino acids and sugar molecules, and this enantioselectivity has been utilized to achieve asymmetric electrocatalytic reduction of carbon dioxide to synthesize various amino acids, mainly serine.<sup>6</sup> The other ChAs<sup>7-10</sup> were speculated to arise from spin polarizations by the asymmetric spin-orbit coupling (SOC) due to the opposite effective magnetic fields induced by electron motion in the antipodal helical structure. Surface-Enhanced Raman Scattering-ChA<sup>7</sup> and Photomagnetic-ChA<sup>8</sup> were applied in enantiomeric quantification with loading of enantiomers on chiral mesostructured Au films. The directional spin control in inorganic helical nanostructures could provide new strategies in quantum technology and theories in photo-electro-magneto-physics.

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## Prodrug-based Nano-delivery Strategy to Improve the Antitumor Ability of SN-38

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Nanometer-sized drugs have been received considerable attention for their potential application as a therapeutic agent for cancer, due to their tumor targeting efficacy. Various types of nanocarriers have been proposed to fabricate nanodrugs. The introduction of drug into nanocarriers, however, would cause several problems, such as low drug loading (less than 10wt%), side effects by themselves, and so on. In order to solve these problems, we have proposed “nano-prodrugs”, which are composed of prodrug molecules without using nanocarriers as a novel designed nanodrugs. In the present study, a series of nano-prodrugs composed of anticancer agent SN-38 and various substituent groups including dimer<sup>1</sup>, fatty acid<sup>2</sup> and cholesterol<sup>3</sup> were synthesized and fabricated using the reprecipitation method<sup>4</sup>. By increasing the hydrophobicity of the prodrug molecule (calculated logP values exceeded ca. 7) through changing the substituent group, the hydrolysis susceptibility of SN-38 nano-prodrugs in mouse serum was drastically decreased, thus prolonged the blood retention time of the nano-prodrugs. In light of this knowledge and the dispersion stability in aqueous media, SN38 nano-prodrugs modified with cholesterol (SN-38-chol NPDs) was selected to be the optimal candidate. The *in vivo* pharmacological effect of SN-38-chol NP was about 10 times higher than irinotecan, the clinically used solubilized prodrug analog of SN-38. In addition, SN-38-chol NPDs shows low side effects with respect to intestinal damage.

In conclusion, we have succeeded in synthesizing SN-38 prodrug and fabricating the corresponding nanoparticles, that is, nano-prodrugs. The nano-prodrugs possess great potential for clinical application and promise to be a next-generation of drug for cancer treatment.

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## Miura-Ori Structured MXene Electrode: A Breathable Solution for Biosensing

**Tzu-En Lin,<sup>ab</sup> Chih-Ning Tsai<sup>b</sup> and Pei-Wen Yang<sup>a</sup>**

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MXene, a two-dimensional nanomaterial made up of transition metal carbides, nitrides, or carbonitrides, has recently been developed. Its general formula is  $M_{n+1}X_nT_x$ , with X being C or N, M being a transition metal, n ranging from 1 to 3, and Tx indicating different surface functional groups. MXene is typically produced through a selective etching process of A-layer atoms in the MAX phase. It has found extensive utility in sensor technology, including biosensors, due to its impressive physical and mechanical characteristics, superior electrical conductivity, and nanostructure, which enhance the sensitivity, conductivity, and catalytic efficiency of sensors. In our current research, we introduce a breathable MXene electrode, built on the Miura-ori pattern, for capturing electromyographic (EMG) signals on the skin surface. Benefiting from the Miura-ori design, these MXene-based electrodes offer exceptional breathability and low, consistent electrode-skin interface impedances, promoting reliable, long-term electrophysiological tracking. Traditional wet Ag/AgCl gel electrodes suffer from an increase in impedance between the electrode and skin due to the slow drying of the electrolytic gel on top, which inhibits sweat evaporation and affects signal gathering. Consequently,

our innovative electrode design presents an appealing solution for capturing high-quality sEMG signals, useful in evaluating physical activities like swallowing.

## Unlocking the Power of Biocatalysis with Reticular Chemistry

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Biocatalysis plays key functions in biological signal transduction and metabolic pathways and have also attracted significant interest in the field of fuel cells, biosensors, disease diagnostics and the synthesis of pharmaceuticals. Despite the unprecedented selectivity and reactivity of enzymes as compared to synthetic catalysts, significant hurdle still remains for the full utilization of biocatalysts for commercial-scale applications. The ability to control catalysis on-demand while expanding their operational conditions is crucial to enable sustainable and efficient biocatalytic reactions.

In this talk, I will highlight some of my group's recent efforts in the design and engineering of biocatalytic nano/micro systems through reticular chemistry. By advancing a fundamental understanding of the molecular-level interactions between the soft biocatalysts and functional matrices, we have engineered nano-bio systems with predictable and tuneable physical and chemical properties for sustainable engineering applications, to address emerging challenges in biomedicine, energy, and the environment.[1-15]

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## Design and Characterization of a Nanodrug-Loaded, ROS Scavenging Hydrogel for Retinal Tissue Repair.

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Reactive oxygen species (ROS) have been identified as common contributors to the pathogenesis of retinal diseases, making oxidative stress a critical aspect of retinal tissue damage. In order to address this challenge, the objective of this study is to develop an injectable hydrogel with antioxidant properties for retinal tissue engineering. By targeting the elevated levels of ROS observed in conditions like retinal stroke and glaucoma, this hydrogel aims to mitigate oxidative stress and provide a potential solution for retinal tissue regeneration.

To achieve this objective, a novel gelatin-modified hydrogel (GelCA) was synthesized. Gelatin, known for its biocompatibility, biodegradability, and ability to mimic the extracellular matrix (ECM), served as the base material. By incorporating cinnamic acid (CA) functional groups into gelatin, the resulting hydrogel can undergo crosslinking through photodimerization and possesses the ability to adsorb lipophilic compounds due to the presence of lipophilic functional groups. Furthermore, GelCA exhibits excellent mechanical properties, making it a suitable material for injection via a syringe.

Moreover, dopamine nanoparticles loaded with curcumin (Cur@PDA NPs) were incorporated into the GelCA hydrogel to enhance its functionality. Curcumin, a lipophilic compound derived from turmeric, exhibits antioxidant and anti-inflammatory properties. The incorporation of these nanoparticles into the hydrogel provides additional benefits, such as reducing oxidative stress and cellular inflammation in the presence of this hydrogel.

In summary, the present study has successfully engineered a multifunctional hydrogel, namely Cur@PDA@GelCA, for retinal tissue engineering applications. By incorporating curcumin-loaded dopamine nanoparticles into the hydrogel matrix, this innovative design demonstrates remarkable potential in mitigating oxidative stress in retinal injury models. The ability of the hydrogel to effectively address this crucial aspect holds great promise for advancing the field of retinal tissue engineering and holds potential for therapeutic interventions aimed at promoting tissue regeneration and functional recovery in retinal diseases and injuries.

## Long-lived Neural Interfaces with Implanted Bioelectronics and Microfluidics

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Complications and traumas resulting from neurological disorders such as Parkinson's disease, traumatic brain injuries, and spinal cord injuries hinder the recovery of the patients [1]. In this work, we explore the opportunities of our first long-lived active neural interface devices that are ultrathin, flexible, implantable, and highly biocompatible. Current long-term implanted electronics mostly relies on rigid, needle-like electrodes to interface with soft tissues, causing foreign body responses that impedes the effectiveness of treatments using implanted devices. Another challenge for implanted bioelectronics is the instability for prolonged operations in relatively corrosive biofluids. As such, implanted devices and their degraded by-products can activate immune responses, leading to inflammation, and this in turn further accelerates the degradation of the implant. Moreover, the cytotoxicity of the leaching ions and fragments from implanted devices can cause more side effects reducing their efficacy. Our preliminary work indicates that coating nano thin SiC layers forms simultaneously a bio barrier preventing ion diffusion and active electrodes for electrical interfaces [2,3]. This approach not only significantly improve device lifetime, but also enhance device efficacy [4,5]. Together with the integration of flexible microfluidics for temperature management, the proposed device

technology can offer combined pain inhibition and tissue regeneration during the treatment of neuronal dysfunctions.

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## Biomass-derived Carbon Quantum Dots as Bioimaging Agents

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Semiconductor nanocrystal, or quantum dot, is among the most exciting discoveries from the nanotechnology field. The size of a quantum dot typically ranges from 1 to 10 nm. Such strong size dependencies facilitate fine-tuning the quantum dot emission wavelength over almost the entire visible spectrum. This fantastic attribute of quantum dots makes them ideal substitutes for conventional organic fluorophores. Over the past few years, rapid progress has been made in developing a new generation of carbon quantum dots (CQDs). These dots have caught the attention of many due to their various benefits, such as their easy preparation, affordability, small size, compatibility with living organisms, bright luminescence, and potential applications in fields like bioimaging. One promising method of CQDs synthesis is using biomass waste as a low-cost and sustainable precursor. Using biomass waste as a precursor for CQDs synthesis provides an environmentally friendly and sustainable alternative to traditional methods. The resulting CQDs have potential applications in various fields, including bioimaging.<sup>1</sup> Carbon quantum dots (CQDs) are a type of metal-free quantum dot that has gained significant interest as a potential alternative to traditional semiconductor quantum dots. One of the reasons for this is their exceptional optical absorptivity, chemical stability, and affordability. Moreover, they are non-toxic and can be easily synthesized from various natural materials, including biomass waste. CQDs' surface can be modified with polar functional groups like carboxyl, amine, and hydroxyl. These groups can be combined with biomolecules for bioimaging or other biological purposes. CQDs can be created using natural or synthetic techniques, such as laser ablation, electrochemical carbonization, hydrothermal treatment, and microwave irradiation. Among these methods, the hydrothermal process has been used in this study to prepare the CQD. An abundance of precursors can be used to prepare CQD via a bottom-up approach ranging from the simplest and most natural molecules to complex and expensive compounds.<sup>2</sup> Here, we reported the preparation of the CQDs obtained from biomass waste and their application in bioimaging. The synthesis process involves a simple one-pot hydrothermal method that utilizes biomass waste as a carbon source, eliminating the need for expensive and toxic reagents.

The resulting CQDs exhibit tunable fluorescence and excellent biocompatibility, making them suitable for bioimaging applications. Hence, biological evaluation studies in cell lines (HeLa, Cardiomyocyte, and iPS) and medaka fish (eggs and larvae) have demonstrated the successful application of biomass-derived CQDs.

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## Innovative Composite Graft of Tricalcium Phosphate and Magnesium Promotes Angiogenesis in Bone Regeneration

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Orthopedic surgeons face a significant challenge when dealing with extensive bone defects. The utilization of autologous or allograft bone grafting falls short in achieving optimal bone fusion. The prevalent approaches in clinical practice for bone reconstruction encompass the Induced Membrane Technique (also known as the Masquelet technique) and Distraction Osteogenesis. However, these methods are time-intensive processes for achieving bone union. While the employment of growth factors such as bone morphogenetic protein 2 (BMP-2) is effective for enhancing bone healing, it comes at a high cost. Research has substantiated that a shortage of magnesium triggers inflammation and impedes the angiogenesis process. Introducing magnesium ions emerges as a pivotal strategy for promoting angiogenesis. This study endeavors to engineer biomedical materials capable of enhancing bone repair and suitable for addressing substantial bone defects. The primary constituents of these materials include tetracalcium phosphate (TTCP) and calcium dihydrogen phosphate monohydrate (MCPM) powder, magnesium powder, and collagen. The gathered data indicates that the sub-micron CPC powder, composed of a ratio of tetracalcium phosphate/monocalcium phosphate monohydrate (TTCP/MCPM; 3.5:1), exhibited a setting time of under 15 minutes and a compressive strength of  $4.39 \pm 0.96$  MPa. These findings demonstrate that the sub-micron CPC powder had a suitable setting time and adequate mechanical strength. Furthermore, an analysis of particle size, composition, and microstructure was conducted. Additionally, the biocompatibility of the sub-micron CPC sponge, which included magnesium, was explored. This examination revealed enhanced cell proliferation and osteogenic induction effects without any harmful effects on cells. Furthermore, the (Calcium phosphate bone cement sponge) CPC sponge containing magnesium facilitated the process of angiogenesis. To conclude, we have introduced a groundbreaking CPC sponge with the potential to serve as a promising material in bone regeneration for extensive bone defects.

## Effects of Negatively Charged Colloidal Clay Particles on the Spectroscopic Properties of Anionic Dyes without Adsorption

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Aqueous colloids of smectite-type clay minerals have been utilized as heterogeneous media of photofunctional dyes because negatively charged clay particles immobilize cationic dye molecules. However, we demonstrate impacts of negatively charged hectorite clay particles on the spectroscopic behavior of anionic dyes [1]. Eosin B dye dissolved in aqueous clay colloids ( $7 \times 10^{-6}$  mol L<sup>-1</sup> dye, 1–30 g L<sup>-1</sup> clay) of synthetic saponite (Sumecton) and hectorite (Laponite) exhibited spectroscopic behavior reflecting the clay particles. The absorption and fluorescence maxima were red-shifted with increasing the clay concentration. Removal of the clay particles by ultracentrifugation recovered the spectra of aqueous solution. When an anionic porphyrin (5,10,15,20-Tetrakis(4-sulfophenyl)porphyrin;TPPS<sup>4-</sup>) was employed, spectral profiles of absorption and fluorescence were altered in clay colloids of the synthetic saponite, depending on the clay concentration (1–30 g L<sup>-1</sup>) similarly to the case of Eosin B. This dependence of the clay concentration was similarly observed at different TPPS concentration from  $1 \times 10^{-5}$  to  $1 \times 10^{-7}$  mol L<sup>-1</sup>. Hence, the effects of the clay colloids should be explained not by reductionistic understanding of clay–dye molecular interactions but by holistic recognition of clay colloids as continuum.

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## Towards Quantum Control of a Room Temperature Mechanical Resonator

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It is now possible to engineer the quantum state of macroscopic mechanical resonators. This opens up the possibility for new quantum technologies, such as quantum-enhanced sensors and quantum memories/interfaces for quantum computers. However, ultrahigh vacuum or cryogenic environments are currently required, limiting the breadth of applications.

In this presentation I will introduce a new approach to control the quantum state of a macroscopic mechanical resonator via measurement and conditioning [1,2]. This approach is based on continuous position measurement, but – unlike other schemes – operates with a measurement that is faster than the mechanical oscillation. By operating in this regime, beyond the usual rotating wave regime, it is possible to prepare quantum squeezed states of motion. Remarkably, our theory predicts that the experimental requirements are greatly relaxed, even compared to mechanical ground-state cooling, to the point that quantum state preparation is feasible at room temperature with existing technology.

I will present experiments showing a classical version of the predicted squeezing effect in a new engineered double-disk optomechanical device fabricated on a silicon chip [3]. These experiments take advantage of both structural damping – which we show that, compared to the usual viscous damping, can improve quantum state preparation – and arrays of mechanical modes. Specifically, I will present experiments demonstrating that continuous position measurement can prepare thermomechanical squeezed states of motion, and to this for ensembles of structurally damped mechanical resonances.

Together, our results provide a new way to generate nonclassical states of macroscopic mechanical oscillators and open the door to quantum sensing and tests of quantum macroscopicity at room temperature.

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## Physical Sensing Effect in SiC-on-Si Heterojunction for Enhanced Performance of Microsensors

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The recent advancements in semiconductor thin films and microdevices have uncovered their potential in shaping the next generation of electronics and sensors for the Internet of Things (IoT) and significantly contributing to the evolution of Industry 4.0 <sup>1</sup>. Among the latest generations of semiconductors, silicon carbide (SiC) dominates applications that require to work at high temperature, high voltage and radiation, and corrosion, making it one of the most preferable material candidate for the future microelectronics and microsensors <sup>2,3</sup>. SiC showcases this potential when grown on Si substrates owing to the excellent crystal material quality, large-area growth capabilities and low manufacturing costs.

SiC boasts a centrosymmetric cubic structure, typically showing a considerable sensing performance in conventional physical effects and methods. This preference has been demonstrated in our prior works on piezoresistive and thermoresistive effects <sup>2,3</sup>. We have uncovered the significant sensing performance of SiC cubic crystalline structure, exemplified by a substantial gauge factor (GF) ranging from 10 to 30 <sup>4,5</sup>. (GF refers to the change of electrical resistance corresponding to the applied strain). In additionally, we have measured the thermoresistive sensitivity of distinct SiC material morphologies (e.g. single crystalline and amorphous) <sup>6,7</sup>. Our evaluations yielded a temperature coefficient of resistance (TCR) spanning from 1,000 to 16,000 ppm/K, depending on semiconductor types and doping levels <sup>6,7</sup>. (TCR refers to the change of electrical resistance corresponding to alternations in temperature).

Recently, we have achieved a significant enhancement in the sensing performance of electronics and sensors through the utilisation of the SiC-on-Si heterojunction <sup>8,9</sup>. This advancement exceeds the capability of conventional sensing devices by coupling two or more distinct physical sensing effects. This innovation shows the potential in opening a new avenue of advancement in the performance of electronics and sensors, presenting in an example of opto-thermotronics <sup>8</sup> and thermo-phototronics <sup>10</sup>. We have found the light harvesting capability of SiC-on-Si, a feature that holds promise for the development of self-powered microsensors and microelectronic devices <sup>11,12</sup>. In this work, we first introduce the fundamentals of various physical sensing effects, including piezoresistance and thermoresistance. Subsequently, we present the recent advancements that contribute to the understanding of the sensing properties and the interplay of physical sensing within a SiC-on-Si heterojunction.

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## Hydrogen Assisted Functionalization of Tungsten Disulfide Nanoparticles

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Implantation of atoms in solid materials provides a way to modify their properties. Our recent approaches of using hydrogen activated by microwave or radiofrequency plasma dramatically increased the efficiency of its adsorption making WS<sub>2</sub> a good candidate for solid state hydrogen storage media [1,2]. To get insight on the chemical configuration, we combined the experimental analysis methods with theoretical modelling based on the density functional theory (DFT). Micro-Raman spectroscopy was used as a primary tool to elucidate chemical bonding of hydrogen and to distinguish between chemi- and physisorption. Hydrogen adsorbed in molecular form (H<sub>2</sub>) was clearly identified in all the plasma-hydrogenated WS<sub>2</sub> nanoparticles samples, both experimentally and using DFT modelling. DFT provides an efficient and practical workbench to investigate the interaction of molecular and atomic hydrogen with WS<sub>2</sub> nanoparticles [3]. It shows that molecular H<sub>2</sub> physisorbs on the surface of those materials on top of W atoms while atomic H may chemisorb on top of S atoms. Diffusion of H<sub>2</sub> on the surface of WS<sub>2</sub> encounters small activation barriers and agrees with the observed dependence of H<sub>2</sub> concentration with temperature.

Intercalation of H<sub>2</sub> between adjacent WS<sub>2</sub> layers revealed an endothermic behavior due to interlayer expansion. A remarkable result, however, is that the presence of a full H<sub>2</sub> monolayer adsorbed on top of the first WS<sub>2</sub> layer of a WS<sub>2</sub> multilayer system strongly facilitates the intercalation of H<sub>2</sub> between WS<sub>2</sub> layers underneath. This phenomenon opens a new gate to implant foreign species inside the nanoparticles. Implantation of layered WS<sub>2</sub> nanoparticles with metal atoms like Ga, Nb, and Re is a promising technique, because it can change the electronic (semiconductor to metal), magnetic (diamagnetic to paramagnetic), and optical properties, the surface characteristics, and the mechanical and chemical behavior of these materials. However, bombarding WS<sub>2</sub> multilayered nanoparticles and nanotubes with focused ion beams of Ga<sup>+</sup> ions at high doses, larger than 10<sup>16</sup> cm<sup>-2</sup>, leads to drastic structural changes, followed by amorphization and recrystallization of the material. Even at lower doses, implantation of Ga atoms was only observed in partially amorphized nanoparticle samples, and the amount of implanted Ga was very small. A substantial increase in the concentration of implanted Ga was observed in nanoparticles previously hydrogenated by a radio-frequency activated hydrogen plasma. DFT calculations reveal that the implantation of Ga in the spaces between adjacent layers in pristine WS<sub>2</sub> nanoparticles is very unfavorable due to the high barriers to expand the interlayer distances. In contrast, in the hydrogenation step, hydrogen molecules are able to intercalate in between adjacent WS<sub>2</sub> layers of the nanoparticles, leading to some expansion of the interlayer distances that in practice eliminates the activation barrier for Ga implantation, and consequently facilitates the implantation of these atoms in the irradiation experiments.

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## Dynamic Configurations of Metallic Atoms in Liquid State for Selective Propylene Synthesis

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The use of liquid gallium (Ga) as a metal solvent, can enable access to well dispersed catalytic metals, at elemental levels, in a liquid state, providing a platform to explore the unique catalytic phenomena. However, how these liquid metallic atoms synergistically facilitate the catalytic reactions and the fundamental differences between the liquid atoms and their solid counterparts need be carefully explored.

The understanding of liquid metal dispersions at the atomic level is essential to unlock their catalytic powers. To gain mechanistic insights into liquid metal catalysts, a GaSn<sub>0.029</sub>Ni<sub>0.023</sub> liquid alloy was investigated for selective propylene synthesis. Originating from their mobility, the positioning of dispersed atoms in a Ga matrix generates configurations where interfacial Sn and Ni atoms allow for critical alignments of reactants and intermediates. Computational modelling suggests a particular configuration, with Sn protruding from the interface and an adjacent Ni below the interfacial layer, could align precisely with a model hydrocarbon, decane, facilitating the propylene production. The reaction pathways were further applied to canola oil with a propylene selectivity of ~94.5%. This research offers a fresh interpretation of and potential practical applications for liquid metal catalysts.

## Electron Modulation of Cu-based catalyst for Electroreduction of CO<sub>2</sub> towards C<sub>2+</sub> Products

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The development for electroreduction of carbon dioxide (CO<sub>2</sub>) is crucial for achieving sustainable cycles and carbon neutrality. Electroreduction of CO<sub>2</sub> to C<sub>2+</sub> products not only mitigate environmental issues by reducing CO<sub>2</sub> but also provide high-value chemicals for modern industry. It is ideal but still challenging by using a facile way to realize high activity and product selectivity in the process of electroreduction of CO<sub>2</sub>.

First, we synthesized CuO nanosheets (CuO NS) via simple hydrothermal method and modified its electron structure by in-situ boron doping to produce B-CuO NS catalyst. The XPS spectra revealed the success doping of B into CuO NS, which obviously changing the electron density of Cu on the surface CuO NS. As a result, B-CuO NS displayed a higher performance for electroreduction of CO<sub>2</sub> compared with original CuO NS. The optimized B-CuO NS catalyst exhibits a Faradaic efficiency of 54.78% for C<sub>2+</sub> production at -1.2 V (vs. RHE). Based on the structural characterization and DFT calculations, the introduction of B increases the charge density of Cu, which could process free electrons to adsorbing \*CO. Thanks to the easier adsorbing of \*CO on B-CuO NS as well as the lower adsorption energy of \*CO on Cu, C-C coupling reaction was promoted to produce more C<sub>2+</sub> products.

Second, we designed a simple anionic species-induced strategy for the efficient electrochemical production of C<sub>2</sub>H<sub>4</sub> from CO<sub>2</sub>. Enlightened by theoretical screening, the specific adsorption of iodide ion (I<sup>-</sup>) on Cu surfaces effectively tunes the adsorption behavior of key intermediates through redistribution the local charge, which in turn facilitate the CO<sub>2</sub> reduction kinetics. When 0.1M CsI is used as the electrolyte, the C<sub>2</sub>H<sub>4</sub> faradaic efficiency of 52% is achieved over a copper/carbon composite catalyst (Cu-NC-600), which is higher than the performance obtained in CsCl and CsHCO<sub>3</sub>, respectively. Density functional theory calculations further reveal that the I<sup>-</sup> as an electronic regulator, facilitates the slow rate-determining step of \*CO protonation, resulting in a much smoother C-C coupling for ethylene production. This study opens up a

new perspective for enhancing the selectivity of the electrocatalytic CO<sub>2</sub> reduction via elaborately selecting suitable anionic species in electrolyte.

Furthermore, we synthesized the heterogeneous structured Cu<sub>2</sub>O/Cu by electrochemical deposition using the top-down strategy. Cu<sub>2</sub>O/Cu catalyst exhibits a Faradaic efficiency of 68.54% for C<sub>2+</sub> production at -1.4 V (vs. RHE). The results of in situ FT-IR spectroscopy and DFT reveal that this heterostructure can reduce the Gibbs free energy of intermediate of COO to COOH compared to pure copper catalyst. It is more beneficial to promote the formation of C<sub>2+</sub> products by reducing the energy barrier of adding H. This heterostructure can also change the adsorption capacity of Cu adsorption site for CO<sub>2</sub> intermediates, thus promoting the formation of multi-carbon products. The kind of self-supporting catalyst synthesized in situ has the characteristics of short synthesis time and low energy consumption. This study provides a new idea for the research and application of electrocatalytic carbon dioxide reduction in carbon neutrality.

### **Biogenic Silver Nanoparticles Capped with *Phoenix dactylifera* L. Seed Extract: Synthesis and its Promising Antimicrobial Activity against *Staphylococcus epidermidis* and *Escherichia coli***

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One type of nanoparticle that has garnered significant attention among researchers in various domains, ranging from agriculture to medicine, environmental preservation, and engineering is the silver nanoparticles (AgNPs). However, the conventional chemical synthesis of AgNPs (c-AgNPs) often involves the use of hazardous solvents, rendering them less suitable for medical applications. Therefore, there has been a concerted shift towards the green synthesis of AgNPs employing plant-based approaches, which provides bio-reducing capping agents and stabilizers for the development of nanoparticles catering to diverse downstream applications. Herein, this study reports an efficient and eco-friendly synthesis of silver nanoparticles using ethanolic *Phoenix dactylifera* L. Medjool seed extract (Md) and highlighting its function as a potent antibacterial agent against 2 wound infecting bacteria, Gram-positive, *Staphylococcus epidermidis* and Gram-negative, *Escherichia coli*. The successful silver nitrate AgNO<sub>3</sub> reduction to Md-AgNPs was evident through visual observation on the change in solution color, shifting from light brown to dark brown and further validated by a UV-Vis surface plasmon resonance (SPR) peak at ~ 450 nm. Zetasizer technique used to characterize the biosynthesized nanoparticles revealed the average size, zeta potential and poly-dispersity index (PDI) of Md-AgNPs were at 78.04 ± 0.56 nm, -59.57 ± 0.23 mV and 0.23 ± 0.004, respectively. The successful biosynthesis of Md-AgNPs, with a size below 100 nm and a negative zeta potential less than -30 mV, ensures minimal harm to cells, excellent stability, effective particles repulsion, while demonstrating monodispersed nanoparticle (PDI < 0.5). The minimal inhibitory concentration (MIC) and minimal bactericidal concentration (MBC) confirms outstanding antimicrobial activity of the synthesized Md-AgNPs on *S. epidermidis* and *E. coli*, comparable to the commercial gentamycin antibiotic. Specifically, MIC was noted at 19 µg/mL and 39 µg/mL, while MBC value of 39 µg/mL and 78 µg/mL were attained for *S. epidermidis* and *E. coli*, respectively. Similarly, Md-AgNPs inhibits the biofilm formation by both the bacteria by more than 50 % to 88 % across concentration of Md-AgNPs ranging from 1\*, 2\* and 4\*MIC. The present effort affirms that AgNPs synthesized through extracts of date seeds as a promising candidate for antibacterial agent.



## Mesoporous Metal Oxide and Metal Pyrophosphate Thin Film Electrodes: Fabrication and Their Electrochemical Properties.

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Mesoporous metal oxides (MMOs) of earth-abundant elements and metal pyrophosphates (MMPPs) are highly important for the development of electrochemical energy applications (such as supercapacitors, electrocatalysis and photo-electrocatalysis). We employ molten-salt assisted self-assembly (MASA) process<sup>1,2</sup> to fabricate MMO<sup>3</sup> and MMPP<sup>4,5</sup> thin film electrodes on various substrates and demonstrate their performance in oxygen evolution reaction (OER) and capacitive properties in alkali media. These electrodes are characterized using diffraction (XRD), spectroscopy (ATR-FTIR, XPS, and EDX), N<sub>2</sub> adsorption-desorption, imaging (SEM and TEM), and electrochemical (CV, CP, CA, GCD) techniques. The mesoporous metal oxide electrodes, fabricated from ethanol solutions, are highly robust and display very low 250, 342, and 642 mV overpotentials at 1, 10, and 100 mA/cm<sup>2</sup> current densities, respectively. We found out that the electrode thickness has no role in the OER performance and can be prepared as thin as tens of nanometers with a good stability and OER performance. The MMPP electrodes are not stable under alkali media and transform to  $\beta$ -M(OH)<sub>2</sub>.<sup>3,4</sup> The size and morphology of the  $\beta$ -M(OH)<sub>2</sub> depend on the K<sub>sp</sub> of the initial MMPPs and determine the charge capacity (CC) and specific capacitance (SC) of the electrodes. The  $\beta$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni<sub>1-x</sub>Co<sub>x</sub>(OH)<sub>2</sub> electrodes display high CC and SC values. However, these values are almost 10 times smaller in the  $\beta$ -Mn(OH)<sub>2</sub>,  $\beta$ -Co(OH)<sub>2</sub>,  $\beta$ -Mn<sub>1-x</sub>Co<sub>x</sub>(OH)<sub>2</sub>, and cobalt-rich  $\beta$ -Ni<sub>1-x</sub>Co<sub>x</sub>(OH)<sub>2</sub> electrodes. Fabrication, stability, characterization, and electrochemical properties of the electrodes will be discussed in this talk.

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## Zeolite Crystallization inside Three-Dimensionally Ordered Nanoporous Cobalt Oxides

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**Introduction:** Mesoporous zeolites show high mass diffusivity and short diffusion path lengths arising from the hierarchical nanoporous structure, which induce improved catalytic, adsorption, and separation performances.<sup>[1]</sup> Among the methods of preparing mesoporous zeolites, the porous structure can be precisely controlled using nanoporous carbon templates. However, an important issue is that zeolite formation outside the template occurs during hydrothermal synthesis,<sup>[2]</sup> which may be due to the hydrophobic

nature of the pore wall surface of carbon. In this study, we propose a novel way to solve the issue by using cobalt oxide ( $\text{Co}_3\text{O}_4$ ) templates instead of nanoporous carbon templates.  $\text{Co}_3\text{O}_4$  is an influential candidate material because  $\text{Co}_3\text{O}_4$  is relatively hydrophilic, hard to dissolve in an alkaline solution under hydrothermal conditions, and easily removed through acid treatment. Silicalite-1 was synthesized inside the nanopores of three-dimensionally ordered nanoporous  $\text{Co}_3\text{O}_4$  to demonstrate the concept above, and mesoporous silicalite-1 was obtained after the template removal.

**Experimental:** Silicalite-1, a typical zeolite, was formed inside the nanopores of the ordered nanoporous  $\text{Co}_3\text{O}_4$  template. The ordered nanoporous  $\text{Co}_3\text{O}_4$  templates were prepared using self-assembled uniform silica nanospheres (silica colloidal crystals, SCCs). Cobalt nitrate aqueous solution was introduced into the interstitial spaces of the SCCs. After drying, calcination, and removal of silica nanospheres, the ordered nanoporous  $\text{Co}_3\text{O}_4$  with fcc-type spherical nanopores was formed. Then, the silicalite-1 precursor solution was infiltrated into the nanoporous  $\text{Co}_3\text{O}_4$  templates, and silicalite-1 was crystallized via hydrothermal synthesis inside the nanopores. Finally, the  $\text{Co}_3\text{O}_4$  templates were removed using an acidic solution, forming mesoporous silicalite-1.

**Results and Discussion:** The formation of silicalite-1 was confirmed by the powder XRD pattern. The peaks assignable to  $\text{Co}_3\text{O}_4$  were not observed, indicating the removal of the  $\text{Co}_3\text{O}_4$  templates. Based on the SEM images, TEM images, and SAXS profile, the formation of the fcc-type ordered mesopores reflecting the porous structure of the  $\text{Co}_3\text{O}_4$  templates was confirmed. The SAED patterns showed single-crystal-like spots, indicating the crystal growth of silicalite-1 inside the template. Suppression of the silicalite-1 formation outside the template was also confirmed by SEM, TEM, and  $\text{N}_2$  adsorption-desorption measurements. These results indicate that the  $\text{Co}_3\text{O}_4$  templates are superior to the conventional carbon templates for precisely controlling the porous structure of mesoporous silicalite-1 via hydrothermal synthesis.

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## Heavy-duty Anticorrosion Coatings Prepared from Epoxy Zinc-rich Composites with Small-loading of rGO to Partial Replacement of Large Amount of Zinc Dust

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Small loading (e.g., 0.5 wt%) of rGO was utilized to replace a large amount (e.g., 20–30 wt %) of zinc dust (ZD) in solvent-based zinc-rich epoxy composite coatings (ECCs) to maintain similar anticorrosion, as well as to promote the adhesion/wear resistance of the corresponding coatings simultaneously. First, the anticorrosion of zinc-rich ECCs containing 20, 40, and 80 wt% of ZDs (denoted as DZ-20, DZ-40, and DZ-80, respectively) was evaluated by performing a series of electrochemical measurements. The anticorrosion of ECCs was found to decrease in the order of DZ-80 > DZ-40 > DZ-20. However, wear-resistance and adhesion tests of ECCs had the opposite trend of DZ-80 < DZ-40 < DZ-20 based on the method of ASTM 3359 and ASTM D4060, respectively. Subsequently, the small-loading of calcined GO at the operational temperatures of 300 °C and 1400 °C (denoted as rGO-300 and rGO-1400, respectively) was further incorporated into ECCs to partially replace large amounts of ZD and maintain similar anticorrosion performance and promote the wear resistance and adhesion of the corresponding ECCs. This finding indicated that introducing a small loading of 0.5 wt% of rGO-300 and rGO-1400 can partially replace 20 wt% and 30 wt% of ZD load, respectively, in ECCs. Accelerated salt-spray corrosion assays of scrapped test panels with and without coatings in an aggressive solution medium were used to evaluate corrosion resistance according to ASTM B-117. Results obtained from the salt-spray assays of ECCs were consistent with those from the electrochemical corrosion measurements.

# Study on the Structure Design and Electrochemical Performance of Nonprecious Metal Catalyst Layer for Fuel Cell

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Proton Exchange Membrane Fuel Cell (PEMFC) has the advantages of low operating temperature, high power design and zero emissions. But the commercialization of PEMFC is limited by the high cost of catalysts<sup>[1]</sup>. In order to improve the preparation efficiency and properties of catalyst, we have adopted an electrodeposition method to rapidly synthesize Fe-N-C catalysts. We dissolved the 2-methylimidazole and ZnCl<sub>2</sub>, FeCl<sub>3</sub> in methanol respectively, and mixed the solutions after completely dissolving<sup>[2]</sup>. After the electrodeposition was completed, the working electrode was taken out and dried in oven. Then the precursors were scraped off from the electric sediment and calcined under N<sub>2</sub> for one hour. The prepared Fe-N-C catalyst was characterized and the catalyst has excellent oxygen reduction reaction performance, the half wave potential can reach 0.75 V vs RHE. The performance of single cell assembled with membrane electrode assembly exhibited the maximum power density of 480 mW/cm<sup>2</sup> under 1 bar back pressure.

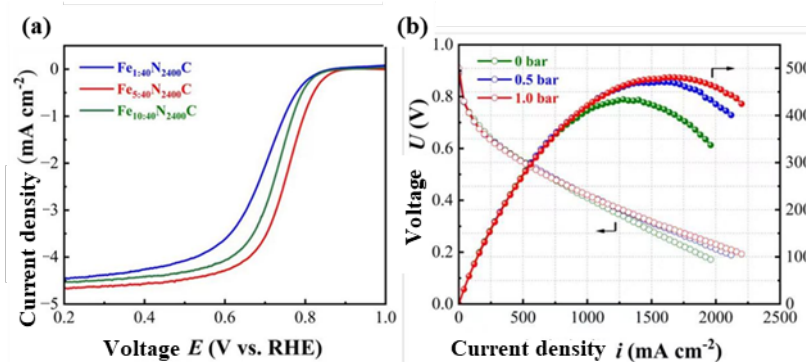


Fig 1. (a) LSV curves of catalysts with different concentration of iron salts, (b) polarization curves and power density curves of MEA different back pressures.

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## Evaluation of the Influence of the use of Aggregates with Different Thermal Expansion Coefficients on the Behavior of Coating Mortar Submitted to Accelerated Aging

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The present work aims to evaluate the behavior of rendering mortars with aggregates with different thermal expansion coefficients when subjected to thermal stresses generated by accelerated aging. Four cementitious rendering mortars have been developed, using natural fine aggregates (AN) and fine aggregates from crushed basaltic rock (ABB), crushed granitic rock (ABG) or crushed quartzite rock (ABQ). The thermal expansion coefficients of the aggregates and the characterization of mortars in the fresh state were

determined. In the hardened state, the rendering mortars were subjected to accelerated aging and analyzed before and after the thermal stress. The evolution of the cracking in the microstructure of the rendering mortars was analyzed by scanning electron microscopy. The results have demonstrated that mortars composed by natural fine aggregate (AAN) have shown a significant degradation when compared to the rendering mortars composed by crushed basaltic rock (AABB), crushed granitic rock (AABG), and quartzite crushed rock (AABQ). The importance of textural parameters and of the thermal properties of the aggregates in the mortar composition has been proven in all rendering mortars made out from crushed rock aggregates, as well as the influence of the superplasticizer used in the increase of the mechanical strength during the accelerated aging.

**Keywords:** fine aggregate thermal gradient. Texture parameters. Rendering Mortar. Accelerated aging.

**Day 2 ABSTRACTS**

**September 28, 2023**

**Session: JST-ERATO Special Session**

### **New Pore Size Control Technique of Mesoporous Gold Films by Electrochemical Synthesis Using Advanced Soft Template Method**

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Mesoporous gold (Au) films with tunable pores are expected to provide fascinating optical properties stimulated by the mesospaces, but they have not been easy to realize because of the difficulty of controlling the Au crystal growth. A reliable soft-templating method to fabricate mesoporous Au films using stable micelles of diblock copolymers, with electrochemical deposition advantageous for precise control of Au crystal growth was reported by our group[1]. An effective way control pore size during preparing mesoporous Au films using soft-templates was controlled by utilizing spherical micelle size control. Therefore, we propose to extend the soft-templating method of forming one mesopore using one spherical micelle as a template, that is the basis of this method, and to form mesopores using one or more controlled number of micelles as a template. So, the controlling the number of micelles in the soft-template can control size of mesoporous. This method can control pore size of mesoporous gold film using same precursor, and the pore size within a mesoporous thin film can be easily changed, and thin films with graduated pore diameters can also be prepared. Usually, deposition behavior was controlled by deposition conditions however they have not been realized yet because of the difficulty of controlling the Au crystal growth. In the electrochemical reaction, the reactivity is controlled by controlling the current or the potential, but because the current and potential of the parameters to be controlled are uniquely determined, it was not easy to control the deposition of gold, which is difficult to control.

Therefore, we designed a cell in which the current and potential can be controlled individually, and controlled the pore size of the mesoporous gold thin film by changing the number of micelles incorporated was investigated with controlling deposition condition. As a result, pore diameter control was achieved by controlling the current while keeping the potential constant. Moreover, the mesoporous film with gradient pore size in horizontal or vertical was successfully prepared. Mesoporous gold thin films with various mesostructures have been fabricated from a same precursor solution using an electrochemical cell in which current and potential can be independently controlled. Mesoporous gold thin films with various

mesostructures have been fabricated from a same precursor solution using an electrochemical cell in which current and potential can be independently controlled. The use of this electrochemical cell is expected to enable the formation of mesostructures that cannot be fabricated using conventional electrochemical processes.

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## Multiscale Organization in Mesoporous Titania Films for Remarkable Optical Anisotropy

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A huge variety of nanomaterials have been synthesized based on spontaneous organization of various building blocks for exploring unprecedented useful functionalities. Porous materials prepared through self-assembly of amphiphilic materials find enormous applications using their remarkable structural features such as extremely large specific surface area. We have studied fine structural control of mesoporous silica films especially on the control of the in-plane alignment of the cylindrical mesopores for the development of anisotropic functionalities ascribed to the structural anisotropy.<sup>1)</sup> If we could expand the available wall-forming materials to nonsiliceous ones, further improved anisotropic properties should be expected reflecting their intrinsic properties. Titania (TiO<sub>2</sub>) is a transparent wide-bandgap semiconductor with a high refractive index, and it has a variety of applications including photocatalysts, optical coatings and cosmetics.

Films of mesoporous TiO<sub>2</sub> can be prepared based on the sol-gel chemistry using amphiphilic block copolymers as a template.<sup>2)</sup> However, control of the in-plane alignment of the mesopores has been a long-time issue, because the formation of a hollow structure and uniaxial alignment had been incompatible so far. Here, we report the first successful preparation of mesoporous TiO<sub>2</sub> films wherein the in-plane orientation of the cylindrical mesopores is entirely controlled. We overcame the above incompatibility by developing a novel technique that allows the alignment control of the lyotropic liquid crystal (LLC) phase consisting of Pluronic P123 and the TiO<sub>2</sub> precursors. We have found that the substrates with a fine wavy cross-section (wavy substrates) prepared by photolithographic procedures allow the alignment of the cylindrical micelles of P123 perpendicular to the grooves.<sup>3)</sup> The controlled alignment is due to the elastic properties of the LLC; the perpendicular alignment to the grooves is energetically the most advantageous configuration.

The mesoporous TiO<sub>2</sub> films with aligned cylindrical mesopores were prepared on the wavy substrates by the dip-coating process thorough the evaporation-induced self-assembly process. The shape of the surface morphology has been optimized for getting a narrow alignment distribution. The block copolymer template was removed by calcination in air at 350 °C.

The highly anisotropic structure of the films was confirmed by cross-sectional SEM and 2D-GISAX. The distribution of the in-plane alignment direction of the mesopores was estimated to be ~22° from in-plane XRD. The high magnification TEM images and the wide-angle XRD patterns prove that the TiO<sub>2</sub> in the pore walls are nanocrystals of anatase. Thus, it was demonstrated that the aligned mesoporous TiO<sub>2</sub> films in this study have a hierarchically controlled structure over the multiple length scales, that is, angstrom, nanometer and millimeter ranges.

The optical anisotropy of the films was characterized by the high accuracy universal polarimeter, HAUP,<sup>4)</sup> which enables simultaneous measurements of anisotropies in refractive index and absorption. The refractive index parallel to the alignment direction of the mesopores is higher than that perpendicular to the mesopores

by 0.06. This remarkable birefringence is a consequence of the large refractive index of crystalline TiO<sub>2</sub> and the totally aligned mesoporous structure, and it indicates that the titania films with the aligned mesopores can be applied to optical phase plates.

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## Tailor-made Synthesis of Sulfur-Doped Mesoporous Carbons

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Supercapacitors are used for the rapid storage and release of electric energy because of long life cycle, high power density, and flexibility. Furthermore, supercapacitors are eco-friendly because supercapacitors are indispensable to save the fuel energy. Indeed, supercapacitors are used for hybrid car and portable device. Carbon materials like an activated carbon are used for the supercapacitors. Especially, nitrogen-doped carbon materials prepared from dopamine using the template method are known to show high capacitance because nitrogen atom enhances surface-charge-storage capacity.[1] Recently, sulfur-doped carbon prepared by adding sulfur source is also expected, however, the understanding of effect of sulfur atom is difficult because the synthesis of pure sulfur-doped carbon is difficult. In this presentation, we report the synthesis of pure sulfur-doped carbon without nitrogen atom from dopamine derivative containing sulfur atom using the template method. To understand the effect of sulfur atom, we report the structure of sulfur-doped carbon by using scanning electron microscope, small angle X-ray scattering and X-ray photoelectron spectroscopy and their electrical property.

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## Controlled Growth of large-Sized ZIF-8 Single Crystals Via Solvothermal Method with Effects of Various Temperature.

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Among several zeolitic imidazole frameworks (ZIFs), ZIF-8, in which 2-methylimidazole and Zn ions are arranged regularly, has garnered significant attention due to its unique crystal and pore structures<sup>1</sup>. Various sizes and shapes of ZIF-8 crystals have been reported based on synthesis parameters such as the molar ratio of organic ligands and metal ions<sup>2</sup>, solvent, and temperature<sup>1</sup>. However, the existence of large-scale single-crystal ZIF-8 has not been explicitly reported through photographic evidence. Herein, we present the synthesis of millimetre-sized single crystal ZIF-8 using the solvothermal method in N,N-diethylformamide (DEF). The resulting 1-mm single crystal is grown via the solvothermal method at 120°C for 72 h. The crystal was characterized through N<sub>2</sub> adsorption-desorption isotherms, scanning electron microscope (SEM), and other analytical techniques. Additionally, single crystal X-ray diffraction is employed to comprehensively investigate the framework mobility at various temperatures (100 to 500K).

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## Balancing between Porosity and Connectivity: MgB<sub>2</sub> Superconducting Joint Architecture with the Functionality to Screen External Magnetic Fields

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We have reported a superconducting joint architecture to join unreacted C-doped multifilament MgB<sub>2</sub> wires with the functionality to screen external magnetic fields for MRI magnet applications. For producing the magnetic field screening effect, the MgB<sub>2</sub> bulk was formed around the current transfer path within the joint in such a way that it produces supercurrent within to screen external magnetic fields. Two joints were fabricated using 290 MPa (joint 1) and 360 MPa (joint 2) powder compaction pressure. Joint 1 made using 290 MPa compaction pressure exhibited better performance in a self-field compared with joint 2; however, joint 2 exhibited significantly better in-field performance compared with joint 1 due to the magnetic field screening effect. Joint 2 showed the magnetic field screening effect up to 1.5 T ( $I_c$ : 30.8 A) at 20 K and up to 2 T ( $I_c$ : 46.1 A) at 15 K. Both the joints exhibited a  $T_c$  of ~34.3 K in a self-field and a main MgB<sub>2</sub> phase with minor MgO ( $\leq 7.2$  mol %) impurity. The cross-sectional SEM image and EDS elemental maps

showed many voids in the intermediate bulk, with some pores formed close to the interface between the MgB<sub>2</sub> bulk and the MgB<sub>2</sub> core of the filament, and a high concentration of O in the filament core. These two features were attributed to be responsible for the relatively low performance of the joints compared with the bare wire. Finally, the joint fabricated in the closed-loop coil showed a resistance of  $3.32 \times 10^{-14} \Omega$  at 20 K in a self-field, which is low enough for MRI magnet applications. The magnetic field screening effect shown by the joint is unprecedented and expected to be extremely valuable for MgB<sub>2</sub>-based MRI magnet applications, where the  $I_c$  of the joints is lower than the  $I_c$  of the connected wires in a given magnetic field and temperature.

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## Enhanced Light-Matter Interactions in Mesoporous Plasmonic Structures for Advanced Sensing and Catalysis

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Porous plasmonic materials demonstrate strong plasmon resonance enhancement because of a ultrahigh surface area, abundant round surface tips, and pores/voids. The combination of concave and convex features of plasmonic nano-crescent antennae can collect and focus light to generate ultra-strong near fields. Extended arrays of pores in three dimensions should enhance both local and long-range plasmon coupling effects, but little work has addressed this topic.

Mesoporous gold films, nanoparticles, and 3D substrates with a tunable pore size ranging from 5 to 30 nm facilitate mass transport of guest matter leading to a higher number of interaction events between a molecule of interest, plasmonic surface and generated plasmons compared to non-porous ones. We prepared hybrid nanostructures of gold films with AgNPs [1], nanoporous metal-organic framework [2], microporous foam coated by silver mesoporous layer, and porous chiral shuriken structures. These hybrid porous substrates demonstrated an advantageous application for surface-enhanced Raman spectroscopy (SERS) biosensing of thiols in the presence of living cells [1], chiral drug pseudoephedrine [2], microplastic [4] and chiral fungicide metalaxyl enantioselectively. For SERS application, mesoporous architecture serves a filtering function of large biomolecules from biomatrix or environmental matrixes, and achieves the maximum signal enhancement. The mesoporous NPs with different pore's size [3] show advantageous porosity-induced symmetry breaking because strong electric fields of the plasmon are colocalized along concave/convex features where step-edges and kinks in the atomic structure generate numerous catalytic active sites. Plasmon-enhanced photodegradation of metanil yellow was used to demonstrate the superior photocatalytic properties of mesoporous AuNPs. In turn, porous shurikens with large plasmonic density generate strong superchiral field to enantioselective degrade racemic mixture of metalaxyl depending on the chirality of the shuriken.

Mesoporous plasmonic materials interact with matter offering not only an avenue for fundamental exploration but also a conduit for transformative advancements across various disciplines. As the research horizon broadens, we anticipate that porous plasmonic materials will continue to make advances in the field of plasmonic sensing and catalysis.

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## Development of Ordered Honeycomb Vanadium Dioxide Films for Highly Transparent Smart Window Coatings

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Vanadium dioxide (VO<sub>2</sub>) is an attractive material for energy-saving smart windows due to its reversible metal-to-insulator transition (MIT) near room temperature.<sup>1, 2</sup> This thermally induced phase transition is reversible and typically accompanied by a dramatic change in the optical properties in the near-infrared (NIR) region from a low-temperature transparent state to a more blocking state at high temperatures, giving this material with the unique ability to regulate solar heat flux by responding to temperature automatically.<sup>3</sup> As a result, VO<sub>2</sub> nanostructures have attracted significant interest for thermochromic smart windows. However, some issues still remain with regard to the fabrication of VO<sub>2</sub>-based smart windows, such as the low visible light transparency, unpleasant dark to brown appearance, and the difficulty in balancing the solar modulating ability ( $\Delta T_{sol}$ ) and visible light transmittance ( $T_{vis}$ ) without compromising one or the other, thus requiring a proper fabrication design.<sup>4</sup> This work reports a new template-free surface-patterning technique to fabricate ordered macroporous honeycomb-structured VO<sub>2</sub>(M) films. This template-free structure engineering technique can generate ordered two-dimensional (2D) microstructures without the use of soft or hard templates. The resulting ordered VO<sub>2</sub>(M) honeycomb films fabricated via this technique exhibit complex structural hierarchy and the domain size and distribution of these films can be tuned by tailoring the pertinent variables. The optimized ordered honeycomb-structured VO<sub>2</sub>(M) film exhibits a very high  $T_{vis}$  up to 95.4% with a competitive  $\Delta T_{sol}$  of 5.5%. The transition temperature of the ordered VO<sub>2</sub>(M) films can be further enhanced through controlled doping with tungsten. These findings are very important for preparing highly transparent but energy efficient smart windows. The proposed dual-phase transformation method is promising as a scalable surface-patterning technique for achieving high-performance metal oxide coatings with diverse applications, such as catalysis, sensors, and optical and electronic devices.

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## Multicomponent Ultrathin MOF derived Adjustable High Entropy Oxide Nanoparticles

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Controllable synthesis of high entropy nanoparticles with small size and uniform distribution is notoriously difficult, especially via mild reaction conditions. Herein, by incorporating multiple metal nodes into one single MOF, we synthesized an ideal precursor for preparing ultrafine high entropy oxide via moderate heating rate and undemanding condition. So far, we have succeeded in preparing 28 kinds of MOFs with different combinations of metals or different organic ligand, and thus proved the preparation method to be universal and inclusive. The MOFs are startling thin, for which they should be named as MOFene. The strong binding effect between metal nodes and organic ligands in MOF have great stabilizing effect during temperature rising process, which can avoid premature phase separation and render homogeneous mixing of metals at final high temperature. Therefore, high entropy nanoparticles with the smallest size (with an average particle size below 1 nm) have been made only through mild calcination of the MOF. The high entropy nanoparticles are embedded into the MOFene-derived ultrathin nitrogen-doped carbon in-situ, providing super large specific surface area, enormous active sites, as well as quantum effect for reactions. What's more, by mounting high entropy particles in carbon nanosheet, the two parts will greatly benefit from synergistic effect in between, and this structure can expose high entropy sites to reaction environment as much as possible. Promisingly, it can be used in many fields like photocatalysis, electrocatalysis, supercapacitor, etc. We believe that our work can shed light on the advanced preparation of 2D, MOF, high entropy materials, and so forth.

## Session: Materials Science and Engineering

### Persistent Homology Analysis of the Effect of Structure on the Elastic Modulus of Wet Powder Materials

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Wet powders are widely used in various fields, such as ceramics, pharmaceuticals, civil engineering, etc. The mechanical properties of wet powders are strongly affected not only solid properties of the particles but also by their structure, including gas and liquid distribution. Conventionally, the three-dimensional structure of the particle packing structure has been challenging to quantify, and structural inhomogeneity has prevented the theorization of the strength of wet powder compacts. This study aims to clarify the effect of the packing structure of wet powder compact and to investigate a theoretical prediction of compact strength. This study applies persistent homology (PH) to the structural analysis of wet powder compacts. It proposes an equation for the relationship between saturation and elastic modulus based on the index of structural homogeneity. The compacts were prepared by slip-casting using suspensions with various particle size distributions as raw materials. Suspensions were prepared from high-purity alumina powder with a mean particle diameter of 0.7  $\mu\text{m}$  (AKP-15) and 0.2  $\mu\text{m}$  (AKP-50). Compression tests were performed to obtain the relationship between saturation and elastic modulus experimentally. When the volume ratio of AKP-15 ( $V_r$ ) was changed, the elastic modulus tended to decrease at  $V_r 0.3$ . Such a trend didn't observe for bulk density, indicating that bulk density does not simply correlate with the elastic modulus in wet powder compacts. We applied PH to the packing structure of compacts calculated by DEM simulation. PH obtained the index of structural homogeneity, showing the smallest value at  $V_r 0.3$ . A new empirical equation is proposed to predict the relationship between the elastic modulus and the saturation considering structural homogeneity, specific surface area, surface tension, and porosity as the main factors affecting the elastic modulus in the unsaturated state. These results contribute to the theorization of the strength of wet powder compacts.

## Quantitative Characterization and Multimodal Imaging of Materials using Synchrotron-radiation Based Microtomography at PETRA III

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The Helmholtz-Zentrum Hereon is operating the microtomography stations at the beamlines P05 and P07 located at the storage ring PETRA III at the Deutsches Elektronen-Synchrotron DESY in Hamburg, Germany. Monochromatized synchrotron radiation in the photon energy range from 8 to 120 keV is used to apply microtomography as a standardized research tool to investigate low absorbing biological specimen up to high absorbing materials. Attenuation- and phase contrast techniques were optimized for medium sized samples (diameter of 1 mm up to 40 mm) which are routinely applied as user experiments.

Within this talk the recent developments to optimize the throughput, the spatial resolution, and density resolution will be given and demonstrated on selected samples. Furthermore, sophisticated software tools were developed to obtain quantitative results from multimodal data. First results combining high resolution microtomography with diffraction experiments will be presented.

## Local Photons in Hermitian and Non-Hermitian Quantum Optics

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Single-photon wave packets are the fundamental building blocks of the electromagnetic (EM) field. Despite their particle-like nature, single-photon states can be systematically generated with a large amount of control over both their shape and duration. In order to fully characterise these states, quantum physicists routinely make use of a variety of different representations in which to describe single-photon states, each basis having its respective advantages and disadvantages depending on the particular situation or system being considered. Due to the space-varying and irregular nature of many real-life systems, there is a need to develop a theory of local photons [1, 2]. In this representation, localised photonic excitations are the basic building blocks of all photon wave packets, and interact only locally with their surroundings. In the past, theoretically defining a localised photon has proved challenging, and there are several considerable obstructions to achieving this goal. Most significantly, as was first shown by Hegerfeldt [3], localised photon wave packets do not propagate causally. Moreover, the position-dependent excitations of the EM field observables are not orthogonal meaning that they cannot be localised. In this talk I shall describe the origin of these problems and introduce a new local quantisation that overcomes these difficulties [4, 5, 6]. In particular I shall construct an extended Hilbert space of causally propagating excitations and compare two different constructions of locally orthogonal excitations. One of these excitations is orthogonal under the standard inner product of quantum mechanics, whereas the other is only orthogonal under a modified biorthogonal inner product [7]. Modified inner products have recently been adopted in quantum electrodynamics [8], and are strongly connected to a set of what are called pseudo-Hermitian operators [9]. In the context of electrodynamics, this leads to a non-Hermitian quantisation of the EM field. I shall discuss some of the consequences of these two descriptions and demonstrate an equivalence between them.

## Engineering Nanomembrane Semiconductors for Long-lived Bioimplanted Electronics

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Advancements in implantable electronics have been revolutionizing the healthcare sector, owing to their powerful capability for real-time and continuous physiological recording and stimulation. Since such systems involve direct interfaces with surrounding biofluidic environments, maintaining their long-term sustainable operation, without leakage currents or corrosion, is a daunting challenge.<sup>1-3</sup> This talk will introduce a platform utilizing wide-bandgap semiconductors that are synthesized on standard, low-cost silicon substrates and physically transferred onto flexible templates for implant applications.<sup>4-5</sup> The new flexible platform offers several attractive features, such as chemical stability in biofluids, outstanding water barrier characteristics, and extremely low permeability to ions, making it suitable for stable operation with projected lifetimes of many decades in biological environments. The fabrication approach establishes a route to systems well-suited for integration with soft tissues, enabling the development of unusual wide-bandgap semiconducting devices with bendable, foldable, and flexible formats and advanced functional modes.<sup>6</sup> The integration of this platform with other nanoarchitectures (e.g., mesoporous materials) and its application for neural recording and modulation will also be discussed.

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## Testing Geopolymer Concrete Performance in Chloride Environment

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Geopolymer concrete (GPC) is the result of the reaction of materials containing aluminosilicate such as fly ash and Ground Granulated Blast Furnace Slag (GGBFS) with alkalis to produce an inorganic polymer binder. GPC is a Portland cement free low embodied carbon concrete. The major barriers to geopolymer

concrete widespread adoption by the construction industry are concerns about durability and exclusion from current standards. Chemical reactions characterizing alkali-activated binder systems differ drastically from conventional hydration process of Portland cement. Thus, the mechanisms by which concrete achieves potential durability are different between the two types of binders. As a result, testing methods and performance-based requirements for geopolymer must be developed to be incorporated in a performance base standard. In a previous study by the authors, the suitability of ASTM C1202 standard RCPT for geopolymer concrete was assessed using fly ash and/or GGBFS precursors. The ASTM C1202 standard Rapid Chloride Permeability Test (RCPT) failed to measure the charges passed through most of the GPCs tested. A modified version of RCPT using 10V (as opposed to 60V specified by standard ASTM C1202) is proposed, allowing to successfully measure the charges passed through all geopolymer concrete samples. The validation of the modified ASTM C1202 testing method was carried out by comparison with the results obtained on the same geopolymer concretes using the ASTM C1556 chloride diffusion test. A very good correlation was observed between the modified ASTM C1202 and standard ASTM C1556 chloride diffusion test results.

In this study, alternative precursors are considered to assess if the performance-based method can be used for a wider range of geopolymer materials. Various precursors were investigated including different sources of fly ash and GGBFS, calcined clay and ferronickel slag (FNS). Different activators were also considered. Overall, both testing methods show that a minimum of 50% GGBFS in the precursor is required to achieve an acceptable resistance against chloride diffusion when blended with fly ash or FNS. The lowest chloride diffusion coefficients were observed for mixes with more than 75% GGBFS. Calcined clay/GGBFS based geopolymer concretes seem to perform poorly against chloride penetration even if incorporating GGBFS. However, FNS/GGBFS geopolymer concretes can perform well against chloride penetration. Performance-based recommendations are proposed for the modified ASTM C1202-10V testing method. Three performance-based categories were identified: High performance if the charges passing are less or equal to 200 Coulombs, Medium performance if the charges passing are more than 200 Coulombs but less than 600 Coulombs and Low performance if the charges passing are superior to 600 Coulombs. Geopolymer concretes in the High-performance category seem to perform significantly better than the reference OPC concretes which are currently used in chloride environments. As a result, these concretes could be considered suitable for these types of environments without the need for further investigations.

This work is part of the RILEM Technical Committee 283-CAM activities. This paper reports only the results obtained at the University of Technology Sydney (UTS) and The University of New South Wales (UNSW).

## **Nanoarchitected Nanoporous Plasmonic Metals for High-Performance Surface-enhanced Raman Spectroscopy Substrates**

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Nanoarchitected metals have garnered much attention in a wide range of applications such as catalysts, sensors, biomedical systems, and energy-related applications, because of their unique optical/electrical properties, high catalytic activity, a large amount of active catalytic sites, large surface area, and controllable pore structure. Among these applications, high-performance sensors of hazardous molecules such as residual pesticides, air pollutants, and environmental toxicants have become an essential component of health, food safety, environmental protection, and biomedicine for improving the human condition. Traditional sensing methods such as high-performance liquid chromatography, gas chromatography, mass spectrometry, and semiconductor-based gas sensing suffer from intrinsic shortcomings, including long processing times, complicated sample preparation and measurement procedures, and high instrument costs. As a useful sensing tool, surface-enhanced Raman scattering (SERS) can be used because it is a rapid, facile, and powerful spectroscopic technique for molecule detection, with the advantages of high sensitivity, no

labeling, facile sample preparation and testing, and readily available small equipment. Furthermore, SERS can be used to detect all types of analytes (solid, liquid, and gas). In general, the SERS effect is greatly enhanced in hotspot regions generated by nanogaps in plasmonic nanomaterials. Therefore, the design and preparation of SERS substrates with a large number of hotspots induced by plasmonic nanomaterials are required for high-performance SERS sensors. In this presentation, design and fabrication of nanoarchitected metal materials will be introduced for SERS application. In addition, various functional materials and new fabrication technique for high-performance SERS substrates will be presented.

## Session: Energy and Environmental Materials

### Sustainable Manufacturing of Valuable Chemical Commodities

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Electrochemical manufacturing of chemical commodities provides a potentially cost effective, environmentally friendly and energy efficient alternative to the traditional industrial processes. The large-scale deployment of this technology not only requires the development of highly active and selective catalysts with low cost, but also calls for the advance in devices that can effectively translate the lab-based technology to practical applications. In this study, I will first demonstrate some recent progresses in the development of catalyst materials for (i) hydrogen production via water electrolysis and (ii) hydrogen peroxide generation through selective reduction of oxygen. Through carefully tuning the electronic structures of the active sites in catalyst materials, the adsorption of reaction intermediates on these sites can be rationally adjusted, resulting in both high activity and selectivity toward the production of target chemical commodities. Energy devices based on these catalyst materials are then designed and fabricated, which enable the production of valuable chemical commodities ( $H_2$  and  $H_2O_2$ ) with fast production rates as well as high energy efficiency.

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### CD-COOFe<sup>III</sup> Fenton-like Catalytic Activation of H<sub>2</sub>O<sub>2</sub>

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The global wastewater discharge is approximately 71 billion tons per year, an annual increase of 2 billion tons. Fenton oxidation was one of the available advanced oxidation processes in water treatment, and Fenton chemistry were also widely studied in the field of cell apoptosis, geochemistry, tumor therapeutics etc. Fenton oxidation utilizing hydrogen peroxide ( $H_2O_2$ ) and ferrous/ferric [Fe(II)/Fe(III)] ions under acidic condition is effective to reduce the concentrations of targeted environmental contaminants to acceptable levels. Herein, we report the homogeneous carbon dot-anchored Fe(III) catalysts (CD-COOFe<sup>III</sup>) wherein CD-COOFe<sup>III</sup> active center activates  $H_2O_2$  to produce hydroxyl radicals ( $\bullet OH$ ) reaching 105 times larger than that of the  $Fe^{3+}/H_2O_2$  system. The key is the  $\bullet OH$  flux produced from the O-O bond reductive cleavage boosting by the high electron-transfer rate constants of CD defects and its self-regulated proton-transfer behavior

probed by operando ATR-FTIR spectroscopy in D<sub>2</sub>O and kinetic isotope effects, respectively. Organic molecules interact with CD-COOFe<sup>III</sup> via hydrogen bonds, promoting the electron-transfer rate constants during the redox reaction of CD defects. The antibiotics removal efficiency in the CD-COOFe<sup>III</sup>/H<sub>2</sub>O<sub>2</sub> system is at least 51 times large than the Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> system under equivalent conditions. Our findings provide a new pathway for traditional Fenton chemistry. This new strategy enhanced the kinetic of ferric ion reduction and broadened the pH values of the reaction.

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## CeO<sub>2</sub>-Based Catalysts: Their Unique Catalysis for Transformation of CO<sub>2</sub>-Captured Amines to Organic Urea Derivatives

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CO<sub>2</sub> capture and utilization have emerged as a promising approach to mitigating the global warming. In recent decades, instead of toxic phosgene or other carbonyl sources, CO<sub>2</sub> can be considered as an attractive carbonyl source due to its ubiquitous, non-toxic, and incombustible properties, and thus, non-reductive CO<sub>2</sub> conversion to synthesize organic carbonates, carbamates, and urea derivatives has been investigated widely [1]. However, the reported catalytic systems rely on the use of highly-pressurized CO<sub>2</sub>, whose production requires energy-consuming processes such as compression. In this respect, energy-efficient systems for non-reductive CO<sub>2</sub> conversion need to be devised. Amine carbamates are possible substrates for synthesizing organic urea derivatives without requirement of highly-pressurized CO<sub>2</sub>, since amine carbamates can be synthesized via chemical absorption of CO<sub>2</sub> into amines even at ambient pressure, as seen in amine scrubbers installed in chemical plants. Indeed, Choi *et al.* reported the production of organic urea derivatives from amine carbamates with a homogeneous Ti complex catalyst [2]; yet, for the ease of catalyst-product separation and reuse of catalyst, heterogeneous catalysts are preferable. We recently demonstrated the combination of CeO<sub>2</sub> and 2-propanol as a heterogeneous catalyst and solvent, respectively, to be effective for the conversion of ethylenediamine carbamate (EDA-CA), which was synthesized from ethylenediamine (EDA) and CO<sub>2</sub>, into 2-imidazolidinone [3]. However, there are several drawbacks in this system using 2-propanol, e.g., insolubility of EDA-CA in 2-propanol at room temperature, partial thermal decomposition of EDA-CA under reaction conditions, and involvement of 2-propanol that is originally absent in the upstream CO<sub>2</sub>-capturing step. We, therefore, aimed to transform EDA-CA into 2-imidazolidinone in an appropriate solvent EDA due to the good solubility of EDA-CA into EDA even at room temperature. In this contribution, we introduced our recently developed catalytic system relying on the combination of CeO<sub>2</sub> and EDA solvent with both batch-type and flow-type reactors [4,5]. The use of EDA as a solvent not only was beneficial in terms of EDA-CA solubility but also suppressed the thermal degradation of EDA-CA apparently completely, resulting in the higher reaction rate represented by turnover frequency compared to previously reported systems [2,3]. Under the optimized conditions using the fixed-bed flow-type reactor, as high as 94% yield of 2-imidazolidinone was synthesized successfully.

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## Fluorine Substituted Perovskite Oxides Synthesized via Low-Temperature Processing as Electrocatalysts for Oxygen Evolution Reactions

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Electrochemical oxygen evolution reaction (OER) is an important anode reaction for water electrolysis. To date, many studies have been conducted on the development of OER catalysts. Transition metal oxides such as perovskite oxides (PVs), which are composed of alkali-earth metal ions and transition metal ions, have attracted attention since they exhibit high OER activity especially in alkaline solutions even without precious metal elements such as iridium or ruthenium. In previous studies, enhancement of the OER activity of PVs was achieved by the choice of metal cations and their composition. Recently, substituting oxide ions ( $O^{2-}$ ) in PVs with hetero-anions, such as fluorine ( $F^-$ ), was employed to increase their OER activity. The valence state of metal cations in PVs is one of the important determining factors of their OER activity. Therefore, it is expected that certain amounts of F-substitution may be a promising approach to enhance the OER activity of PVs by tuning the valence state of metal cations. In the present study, we synthesized barium (Ba), iron (Fe), and cobalt (Co) oxides  $BaFe_{1-x}Co_xO_{3-d}$  ( $x = 0, 0.1, 0.2$ ) and successfully enhanced their OER activity by broad-range F-substitution using a low-temperature fluorination process.

$BaFe_{1-x}Co_xO_{3-d}$  ( $x = 0, 0.1, 0.2$ ) was synthesized using a sol-gel method modifying a previous report. [1] F-substitution of  $BaFe_{1-x}Co_xO_{3-d}$  was performed by heat-treatment of the mixture of polyvinylidene fluoride (PVDF) and as-synthesized  $BaFe_{1-x}Co_xO_{3-d}$ . [2,3] The OER activity was evaluated using a rotating disk electrode under  $O_2$ -saturated 1M KOH.

In this abstract, we report the results for  $BaFe_{0.8}Co_{0.2}O_{3-d}$  ( $x = 0.2$ , BFCO-20) and a F-substituted sample with an F/Ba ratio of 1 (F/Ba=1.0). Synthesis of single-phase  $BaFe_{0.8}Co_{0.2}O_{3-d}$  was confirmed by powder X-ray diffraction (XRD) pattern. No impurity formation was observed by F-substitution. X-ray absorption near edge structure (XANES) spectra indicated that F-substitution reduced the valence of Co. Cyclic voltammograms for BFCO-20 and F-substituted BFCO-20 revealed that F-substitution enhanced the OER current. The OER current of the F-substituted BFCO-20 was about 3.9 times higher than that of the as-prepared sample at 1.65 V vs. RHE. [4] In the presentation, we will also discuss details of the structural and electrochemical analysis of the samples.

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## Photoelectrochemical Water Splitting Process by Visible-light-absorbing Semitransparent Tantalum Nitride Thin Film Photoelectrodes

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Photoelectrochemical (PEC) water splitting is widely recognized as one of the most promising methods for the production of hydrogen and oxygen using solar energy and water resource.<sup>[1]</sup> One possible design is



the PV-PEC tandem cell that is composed of a visible-light-absorbing semitransparent photoelectrode as the top cell and a PV-grade narrow-bandgap material as the bottom cell that can absorb transmitted light passing through the top cell.<sup>[2,3]</sup>

Tantalum nitride ( $\text{Ta}_3\text{N}_5$ ) has a bandgap energy of 2.06 eV, which is equivalent to an absorption edge wavelength of 600 nm and is a potential candidate for the fabrication of visible-light-absorbing semitransparent photoelectrode for oxygen evolution reaction (OER).<sup>[2,3]</sup>  $\text{Ta}_3\text{N}_5$ -based electrodes are typically prepared by heating a precursor film composed of a material such as  $\text{Ta}_2\text{O}_5$  and/or Ta metal under an ammonia atmosphere at high temperatures close to 800-1000 °C. To overcome such a harsh preparation condition, the  $\text{Ta}_3\text{N}_5$ -based thin film photoelectrodes were required to fabricate on the chemically durable transparent substrates such as n-type GaN-coated sapphire ( $\text{GaN}/\text{Al}_2\text{O}_3$ ) and insulating quartz ( $\text{SiO}_2$ ) substrate.<sup>[4, 5]</sup> With the surface modification by  $\text{NiFeO}_x$ -electrocatalyst for OER, the  $\text{Ta}_3\text{N}_5$  prepared on  $\text{GaN}/\text{Al}_2\text{O}_3$  substrate ( $\text{NiFeO}_x/\text{Ta}_3\text{N}_5/\text{GaN}/\text{Al}_2\text{O}_3$ ) can generate the anodic photocurrent of 7.4 mA  $\text{cm}^{-2}$  at 1.23 V vs. reversible hydrogen electrode ( $V_{\text{RHE}}$ ) under simulated sunlight illumination. This photocurrent density corresponds to 60% of the theoretical limit of 12.4 mA  $\text{cm}^{-2}$  for  $\text{Ta}_3\text{N}_5$ , assuming a quantum efficiency of 100% on water splitting. The semitransparent  $\text{NiFeO}_x/\text{Ta}_3\text{N}_5/\text{GaN}/\text{Al}_2\text{O}_3$  photoanode has a visible-light transparency approx. 70% at a wavelength longer than 600 nm, enabling the construction of PV-PEC tandem cell coupled with  $\text{CuInSe}_2$ (CIS)-based solar cell. The PV-PCE tandem cell composed of the  $\text{NiFeO}_x/\text{Ta}_3\text{N}_5/\text{GaN}/\text{Al}_2\text{O}_3$  photoanode as the top cell and two-series connected CIS element (dual-CIS) as bottom cell equipped with Ni/Pt cathode for hydrogen evolution reaction was investigated. The tandem cell achieves the solar-to-hydrogen (STH) energy conversion efficiency of 9.0% for the initial reaction stage. In addition, the tandem cell retains the STH of 4.0% over 2 h during the PEC water splitting operation.<sup>[4]</sup>

The  $\text{Ta}_3\text{N}_5$ -based thin film photoanodes prepared directly on an insulating  $\text{SiO}_2$  substrate generated the anodic photocurrent ascribable to the OER without inserting a back-contact conducting layer.<sup>[5]</sup> The PEC OER on  $\text{Ta}_3\text{N}_5/\text{SiO}_2$  photoanodes originated from the n-type self-conductivity of the  $\text{Ta}_3\text{N}_5$  thin film related to the intrinsic semiconductor properties. The preparation conditions of  $\text{Ta}_3\text{N}_5/\text{SiO}_2$  can be tuned to the photocurrent density on PEC OER. The correlation between PEC OER performance and the semiconductor properties of  $\text{Ta}_3\text{N}_5/\text{SiO}_2$  will be discussed in the presentation.

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## Dynamic, Single-atom Liquid Noble Metal Catalysts

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Room temperature liquid metals, such as gallium and its alloys, possess a unique combination of metallic and liquid-like properties, making them highly promising in a wide range of fields including functional materials, soft electronics, and biomedicine [1]. Recently, there has been a growing interest in leveraging these liquid metal features in the field of catalysis, as catalysts in their liquid form tend to outperform their solid-state counterparts. This advantage is attributed to the dynamic nature of liquid atoms. Notably, liquid gallium-based mechano-catalytic and tribo-electric catalysts have been developed for carbon dioxide and biofuel conversion [2, 3]. However, the exploration of liquid noble metals such as silver, gold, palladium, and platinum at low temperature has only just begun. Due to their high melting points (above 1500 °C), it has been deemed impossible to practically utilize these metals in their liquid form at moderate to low temperatures. Nevertheless, a recent breakthrough [4] has made it possible to access liquid noble metals

at low temperatures by using gallium as a solvent. By dissolving platinum in liquid gallium, a liquid platinum catalyst can be obtained. Contrary to the supported solid platinum catalyst, the dissolution of platinum in liquid gallium, results in single atom, yet dynamic catalytic sites combined with exceptional electronic properties that exhibit high catalytic activity for a range of reactions including enzymatic, oxidation, reduction, and electrochemical reactions. For example, when tested for the electrochemical methanol oxidation using liquid platinum as the working electrode, the surface platinum atoms in the catalyst system displays a catalytic activity which is three to five orders of magnitude higher compared to any conventional solid platinum catalysts including the single atom solid catalysts. Molecular dynamics simulations performed on such a liquid catalyst system indicate that platinum atoms remain dynamically dispersed in the liquid gallium matrix without forming platinum-platinum bonds and also activate the surrounding gallium atoms toward catalysis. In essence, dissolving noble metals in a liquid metal matrix generates uniform and dynamic catalytic sites with unique electronic properties, laying the groundwork for prospective theoretical and fundamental investigations in this domain.

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## Sustainable Materials for a Clean Energy Future

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The development of sustainable materials using scalable methods that can enable high efficiency solar energy conversion devices to produce electricity and hydrogen fuel is critical for better utilising world's abundant solar resource and accelerating the much-needed renewable energy transition. Copper containing chalcogenide compounds possesses environmentally friendly, non-toxic, inexpensive and earth-abundant constituent elements and exhibits a band gap in the range between (~ 1.0 to ~ 1.8 eV) and high absorption coefficient (~ 10<sup>4</sup> cm<sup>-1</sup>) making them promise in these sustainable energy technologies.

In this talk, I will talk about our recent research advances in the development of copper chalcogenide compounds such as Cu<sub>2</sub>ZnSnS<sub>4</sub>, Cu<sub>2</sub>SnS<sub>3</sub> and their applications in solar energy conversion technologies mainly thin film solar cells and solar hydrogen production. Current bottlenecks and future promising directions will also be discussed.

## Advanced Atomic Catalysts Design for Energy Systems

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Currently, atomic catalysts (ACs) as the frontier research topics have attracted tremendous attention. To supply theoretical guidance for designing novel electrocatalysts, we have carried out a comprehensive

mapping study of graphdiyne (GDY) based ACs. First, we have proposed the “Redox Barrier Model” to quantify the capability of electron exchange and transfer (ExT), which enables the comparison of different AC systems. For the hydrogen evolution (HER) process, we have extended the conventional indicator of proton binding energy to more diverse indicators including chemical binding energy, desorption energy, and electronic structures. For the first time, we have identified GDY-Eu and GDY-Sm as two promising electrocatalysts for HER, which are also verified by machine learning. For the developments of dual atomic catalysts (DACs), we have investigated the formation stability and electronic modulations for all the combinations between transition metals (TMs) and lanthanide (Ln) metals. Due to the electronic self-balance effects by f-d orbital coupling, the combinations between the Ln metals and TMs achieve optimized stability and electroactivity of GDY-DACs. Meanwhile, the introduction of the main group elements enables activations of the electroactivity of GDY. Recently, we have also achieved the applications of GDY-ACs for the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) with a comprehensive reaction pathway mapping of C<sub>1</sub> and C<sub>2</sub> products for the first time, where different metal selections display distinct selectivity and reaction trends. We propose the integrated large-small cycle mechanism to explain the challenges for C<sub>2</sub> product generation and identify the double-dependence correlation with metal and active sites. First-principle machine learning predicts the reaction energy of C-C couplings, where the adsorptions of the intermediates are critical to achieving accurate predictions of multi-carbon products. Therefore, these theoretical explorations have supplied important theoretical insights into the applications of ACs, opening a new avenue for the rational design of ACs for different energy systems.

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### Slow Photon Engineering in Nanoporous Photonic Crystals for Sunlight-Driven Photocatalysis

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Heterogeneous photocatalysis –“photocatalysis”– is a sustainable light-driven process in which clean sunlight energy is transformed into charge carriers when incident photons interact with the surface of semiconductors, which can then be harnessed to drive secondary reactions. Current existing photocatalyst platforms are severely constrained by low generation of charge carriers and inefficient use of the high irradiance spectral regions of the solar spectrum. Recent advances have demonstrated the integration of functionalised nanoporous anodic alumina (NAA) photonic crystals into photocatalyst platforms can overcome these limitations to enhance photocatalytic efficiency in water purification. This study use titanium dioxide (TiO<sub>2</sub>)-functionalised NAA distributed Bragg reflectors (DBRs) featuring precisely engineered photonic stopbands (PSBs) and semiconducting layers of TiO<sub>2</sub> as model optoelectronic platforms to harness slow light for visible–NIR light-driven enhanced photocatalysis. Photocatalytic degradation of a model organic dye, methylene blue, with its absorbance band within the visible spectrum is used as a benchmark reaction to unveil the mechanism of slow light-enhanced photocatalysis in TiO<sub>2</sub>-NAA-DBRs with tunable PSB and thickness of TiO<sub>2</sub>. Comprehensive analysis of the spectral arrangement between methylene blue’s absorbance band and the red edge of TiO<sub>2</sub>-NAA-DBRs’ PSB is used to identify and quantify the mechanistic contribution of slow light in driving this model photocatalytic reaction. Our findings reveal that photodegradation rates rely on both spectral position of PSB and thickness of semiconductor. The performance of these photocatalysts is found

to be maximum when the PSB's red edge is spectrally close to the red or blue edge of the absorbance band of methylene blue, and to dramatically decrease when the red edge of the PSB is positioned at the absorbance maximum of methylene blue due to light screening by dye molecules. Our study also demonstrates that  $\text{TiO}_2$ -NAA-DBRs featuring thicker semiconducting  $\text{TiO}_2$  layers can harvest more efficiently incident slow light by generating additional charge carriers at the surface of the semiconductor. The crystallographic phase of  $\text{TiO}_2$  in  $\text{TiO}_2$ -NAA-DBRs is demonstrated to be critical in determining the performance of these model photocatalyst platforms, where anatase phase provides ~69% superior performance over its amorphous  $\text{TiO}_2$  form. This study provides opportunities towards the development of energy-efficient, safe, and sustainable photocatalysts for environmental remediation and energy generation.

## Perfluorosilanized Nanoporous Interferometers for Real-time Detection of Per-fluoroalkyl Substances (PFAS)

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Per- and polyfluoroalkyl substances (PFAS) are recognized as one of the most toxic compounds to human health and the environment. They are fluorine-containing compounds widely used in a variety of consumer and industrial products such as food packaging, aqueous film forming foams and non-stick cookware. The identification and quantification of PFAS remain challenging due to their chemical diversity, and their inert and optical and chemical nature. Here, we present an optical system based on the integration of perfluorosilane-functionalized nanoporous anodic alumina (NAA) interferometers with reflectometric interference spectroscopy (RiFS) for real-time, label-free detection of self-assembled monolayers (SAMs) of perfluorooctanoic acid (PFOA) as a model PFAS. The fluorous interaction-induced by self-assembly of PFOA molecules with perfluorosilane functional molecules of different length were monitored based on the changes in the effective optical thickness ( $\Delta\text{OT}_{\text{eff}}$ ) of NAA in real-time and in situ. Analysis of key sensing parameters—sensitivity, low limit of detection and linearity—allowed us to determine the most optimal molecular length of perfluorosilanes to maximize immobilization of PFOA onto functional surfaces. The mechanism of PFOA-perfluorosilane interactions was elucidated through the adaptation of Freundlich and Langmuir isotherm models to experimentally-acquired values of  $\Delta\text{OT}_{\text{eff}}$ . This study suggests that the binding between PFOA and perfluorosilanes immobilized onto the inner surface of NAA interferometers occurred through a fluorous interaction-induced Freundlich mechanism. The proposed system was also used to detect the formation of PFOA-based SAMs in different aqueous matrices such as dionized water, tap and river water, demonstrating its potential real-life applicability. This study provides a new insight into the engineering of functional surface chemistries and the harnessing of fluorous interaction to maximize sensitivity and selectivity to PFAS for future deployable systems to detect these emerging toxicants.

## $\text{Co}_3\text{O}_4/\text{NiOH}$ Mixed Oxide Nanoflowers as Highly Active and Durable Anode Materials for High-performance Li-ion Batteries

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Nickel hydroxide-supported cobalt oxide has been extensively studied as a promising cathode material for high-performance lithium-ion batteries (LIBs). Herein, we demonstrated a single-step eco-friendly solvothermal technique for synthesizing high-performance  $\text{Co}_3\text{O}_4/\text{NiOH}$  nanoflowers with varying cobalt oxide content (0, 2.5, 5, 7.5, 10 wt %) and their excellent performance in LIB applications. The synergistic effect between the two materials resulted in improved electrochemical performance, including high capacity,

excellent rate capability, and cycling stability. The electrode fabricated using 5% Co<sub>3</sub>O<sub>4</sub>/NiOH yielded 1538 mAh g<sup>-1</sup> specific capacity at 0.1 Ag<sup>-1</sup>. The high capacity of the nickel hydroxide-supported cobalt oxide is attributed to the redox reaction of Co<sup>3+</sup>/Co<sup>2+</sup> and Ni<sup>3+</sup>/Ni<sup>2+</sup> ions during the charge-discharge process. The incorporation of nickel hydroxide in the cobalt oxide matrix improves the electronic conductivity and facilitates the diffusion of lithium ions, resulting in enhanced rate capability. The stability of the nickel hydroxide-supported cobalt oxide is achieved by preventing the dissolution of active materials and suppressing the formation of the solid-electrolyte interphase (SEI) layer. The synthetic approach adapted for fabricating the porous Co<sub>3</sub>O<sub>4</sub>/NiOH nanoflowers is facile, relatively greener, and low-cost, which can be utilized for fabricating other mixed metal oxide-based microstructures for application in energy storage devices.

**Keywords:** Battery, Cobalt oxide/Nickel hydroxide, Cathode Material, Green synthesis, Nanostructured materials.

## Low-cost and High-safety Aqueous Zn Batteries

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Aqueous Zn batteries (AZBs) have inspired an overwhelming number of literature studies due to their safety, cost effectiveness, and environmental benignity. Directly employing metallic Zn foil as an anode significantly simplifies battery manufacturing and simultaneously broadens the operating voltage window of aqueous batteries, benefiting from its high overpotential against electrolyte decomposition. Nevertheless, serious issues, such as dendrite growth and side reactions, occurring at the Zn/electrolyte interphase, make the Coulombic efficiency and lifespan of Zn metal electrodes far from satisfactory, which has also been motivating new research interest in interfacial engineering to solve these problems. Owing to the rapid evolution of this new area, it is highly desirable to provide current and timely updates of interfacial strategies and their effectiveness evaluation. From the two sides – the electrode and the electrolyte at the interphase – this report thoroughly summarizes our fundamental understanding of interfacial strategies, including designing mechanisms, creating new methods, and technical challenges. Importantly, this report also analyses the effectiveness evaluation techniques for interfacial strategies, including electrochemical methods, characterization measurements, and computational simulations, providing guidelines for the accurate evaluation and analysis of AZBs in the future.

## Construction and Gas Sensing Properties of ZnO-based One-dimensional Heterostructures

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In this study, several types of ZnO-based one-dimensional heterostructures (ZnO-SnO<sub>2</sub>, ZnO-In<sub>2</sub>O<sub>3</sub>, ZnO-NiO, etc.) were synthesized and their gas sensing properties were investigated. For the heterostructures preparation, the ZnO nanowires were firstly synthesized by a hydrothermal method, then, different types of heterostructures were constructed by in-situ growing the second-phase nanoparticles on the surfaces of the ZnO nanowires using different ways based on the chemical properties of the second-phase nanoparticles. The prepared heterostructures showed similar microstructures, their diameters were 30 to 50 nm while the length ranges from 500 nm to several micrometers. The gas sensing tests showed that the heterostructure construction is an effective way to enhance or regulate the gas sensing performance of the ZnO nanowires, but the physical and chemical properties of the additives play an important role in the gas sensing performance of the heterostructures. Furthermore, the gas sensing performance of the pristine ZnO nanowires as well as the heterostructures in the air and in N<sub>2</sub> were compared. It's interestingly found that the sensors showed much higher responses in N<sub>2</sub> than in the air. Finally, the mechanism of the observed gas sensing phenomena is discussed

**Key words:** ZnO, nanowires, heterostructure, gas sensing

## Synthesis of MnS/MnO decorated N, S-doped carbon prepared by the Mn ion-coordinated polymer obtained using a new synthetic method

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In recent years, hybrid organic-inorganic materials have garnered significant attention in both industry and academia. Specifically, three-dimensional (3D) porous coordination polymers, as a carbon precursor, offer numerous advantages, including large active sites and high porosity. In particular, Metal-ion coordination polymers are particularly useful in preparing catalytic materials.

In this study, we synthesized a Mn<sup>2+</sup> coordinated polymer, bonded using a new synthetic method involving a sulfur atom with acetate counter ions (Mn-DTOGA), through an imine formation reaction. Subsequently, by calcinating the Mn ion-coordinated polymer at different temperatures (700, 800, and 900 °C), we prepared MnS/MnO decorated N, S-doped carbon nanoparticles (MnS/O-SNC) for practical catalytic reactions. The prepared Mn-DTOGA and MnS/O-SNC structures are characterized using various physical, chemical, and electrochemical analyses such as FT-IR, MALDI-TOF, XRD, SEM, TEM, etc. The as-prepared electrode using the materials was tested for the electrochemical oxidation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and Bisphenol A (BPA).

The Mn-DTOGA reveals a homogeneous sphere shape having a diameter with an average size, estimated to be ~500 nm. The MnS/O-SNC is also a spherical shape with a particle size of around 350 nm. Among catalysts prepared at different calcination temperatures, the MnS/O-SNC (900 °C) shows the best performance in H<sub>2</sub>O<sub>2</sub> and BPA catalytic oxidation. The XPS analysis demonstrates that the MnO decorated outward N, S-doped carbon nanoparticles mainly function for H<sub>2</sub>O<sub>2</sub> and BPA oxidation. The decomposition potentials of H<sub>2</sub>O<sub>2</sub> and oxidation potential of BPA on the catalyst modified electrode are observed to be +0.40 V and ~+0.35 V, respectively. The prepared catalytic materials displays two dynamic ranges with a detection limit of 0.08 (± 0.02) and 0.17 (± 0.04) μM, respectively.

Conclusively, we designed a new synthesis way to synthesize a coordination polymer as a precursor for carbon catalysts. From calcination of the coordinated polymer, MnS/MnO decorated N, S-doped carbon (MnS/O-SNC) nanoparticles were successfully obtained and examined for catalytic oxidation of H<sub>2</sub>O<sub>2</sub> and BPA. We confirmed that the catalytic performances of the oxidation reaction were mainly related to MnO decorated outside the SNC particles. The results show that it can provide a new direction for further study on catalyst design for the practical applications of catalytic reactions.

## Coupled Al<sub>2</sub>O<sub>3</sub>-Nd<sub>2</sub>O<sub>3</sub>-ZnO and Al<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub>-Ag<sub>2</sub>O Composites Prepared by the Sol-gel Method for the Photocatalytic Degradation of Contaminant Organic Compounds in Aqueous Medium

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New photocatalytic materials with even lower electron - hole recombination rates are needed in order to get high photo-conversion of contaminant organic compounds in aqueous medium not only at low concentration of contaminant but even when their concentrations are high. Regarding to this, we have shown that in spite that alumina is considered as an insulator material, γ-Al<sub>2</sub>O<sub>3</sub> prepared by the sol-gel method showed high photocatalytic activity in the degradation of organic compounds in aqueous medium.

In consequence,  $\gamma\text{-Al}_2\text{O}_3$  can be thought as a good option since it is a material of low cost and it has excellent properties such as high specific surface area and chemical stability. However, it is necessary to decrease the recombination rate of the photo-induced electron - hole ( $e^-$ ,  $h^+$ ) pairs of  $\gamma\text{-Al}_2\text{O}_3$  to improve its photocatalytic activity. A possible way to improve the photocatalytic activity of  $\gamma\text{-Al}_2\text{O}_3$  is by adding lanthanide oxide and by doping it with semiconductor oxides. In this work, coupled  $\text{Al}_2\text{O}_3\text{-Nd}_2\text{O}_3\text{-ZnO}$  and  $\text{Al}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-Ag}_2\text{O}$  composites ( $\text{Al-Nd-Zn-x}$  and  $\text{Al-Ga-Ag-x}$ ; where  $x$  = weight percentage of doping metal oxide semiconductor) were prepared by the sol-gel method and studied in the photodegradation of phenol (80 ppm) and diclofenac (50 ppm). The  $\text{Al-Nd-Zn-x}$  and  $\text{Al-Ga-Ag-x}$  composites were characterized by physical adsorption of  $\text{N}_2$ , XRD, TEM, SEM, transient photocurrent response, Raman, UV-Vis, XPS and PL.  $\text{Al-Nd-Zn-x}$  composites with ZnO concentration in the range 0.8–2.0 wt. % showed high efficiency photoconverting about 90 % of phenol and mineralizing about 75 % of dissolved total organic carbon to  $\text{CO}_2$  at 3 h of UV light irradiation. Whereas,  $\text{Al-Ga-Ag-x}$  with  $\text{Ag}_2\text{O}$  concentration between 1.0 and 5.0 wt. % photoconvert more than 90 % of diclofenac and mineralize about 80 % of dissolved organic carbon at 20 min of reaction. In both cases, the photodegradation reaction kinetics were adjusted well to a first-order Langmuir-Hinshelwood reaction kinetics. The improvement in the photocatalytic activity of coupled  $\text{Al-Nd-Zn-x}$  and  $\text{Al-Ga-Ag-x}$  composites prepared by the sol-gel method with respect to that of pure  $\gamma\text{-Al}_2\text{O}_3$  could be due to the intimate contact between species and the high dispersion of ZnO and ( $\text{Ag}^0$ ,  $\text{Ag}^+$ ) species respectively favoring the separation of photogenerated charge carriers and the decrease in the recombination rate of photogenerated electron-hole pairs. In both materials,  $\text{Nd}_2\text{O}_3$ , ZnO and  $\text{Ag}^0$  and  $\text{Ag}^+$  species act as electron traps, whereas  $\text{Al}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  act as hole traps, promoting the decrease in the recombination rate of photo-induced electron-hole pairs. Transient photocurrent response experiments confirm that ZnO and silver ( $\text{Ag}^0$ ,  $\text{Ag}^+$ ) species effectively increase efficiently the separation of photo-generated ( $e^-$ ,  $h^+$ ) charges. In the case of diclofenac photodegradation, reaction experiments with addition of scavengers indicate that  $h^+$  and  $\cdot\text{O}_2^-$  radicals are the main active species during the photocatalytic degradation using  $\text{Al-Ga-Ag-x}$  photocatalysts. These alumina-based composite materials prepared by the sol-gel method have excellent properties such as high specific surface area and low band gap energy typical of a semiconductor material which make these as promising photocatalysts to be used in the photodegradation of polluting organic compounds in aqueous solution.

## Low-temperature and Highly Enhanced NO<sub>2</sub> Sensing Performance of Au-functionalized WO<sub>3</sub> Microspheres with a Hierarchical Nanostructure

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Hierarchically nanostructured  $\text{WO}_3$  microspheres that had two types of Au functionalization modes (Au-loaded mode and Au-doped mode) were characterized in terms of their microstructure and  $\text{NO}_2$  sensing performance. Pure, Au-loaded, and Au-doped  $\text{WO}_3$  microspheres were synthesized using a hydrothermal method, followed by a dipping method for Au-loaded  $\text{WO}_3$  microspheres. Microstructure characterization indicated that uniform microspheres with 3–6  $\mu\text{m}$  in diameter were assembled from numerous well-defined individual  $\text{WO}_3$  nanorods with a single crystal hexagonal structure. The morphology and size of the  $\text{WO}_3$  microspheres were not affected by the functionalization of the Au nanoparticles, and the W, O, and Au elements were well-distributed in the  $\text{WO}_3$  microspheres. The  $\text{NO}_2$  sensing properties indicated that the Au nanoparticles not only improved the sensor response and reproducibility but also decreased the operating temperature at which the sensor response reached a maximum. Gas sensors based on pure, Au-loaded, and Au-doped  $\text{WO}_3$  microspheres exhibited a linear relationship between the sensor response and  $\text{NO}_2$  concentration. The sensing performance was significantly enhanced in the following order: pure, Au-loaded, and Au-doped  $\text{WO}_3$  microspheres. This result is due to the modulation of the depletion layer via oxygen adsorption as well as chemical and electronic sensitization of Au nanoparticles.

## Cobalt phthalocyanine-based Conjugated Polymer as Electrocatalyst for CO<sub>2</sub> Reduction to Ethanol

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Electrocatalytic conversion of carbon dioxide to high value-added chemicals is a promising method for solving the energy crisis and global warming. Electrochemical active metal-containing conjugated polymers have been widely studied for heterogeneous carbon dioxide reduction. Here, a stable cobalt phthalocyanine-based conjugated polymer was designed and synthesized for electrocatalysis of carbon dioxide reduction to liquid products in an aqueous solution. Cobalt phthalocyanine were used as building blocks connected with 1,3,6,8-Tetrakis(4-formyl phenyl)pyrenes via imine-linkages, leading to mesoporous formation polymers with the pore size centered at 4.1 nm. Also, the central cobalt atoms shift to a higher oxidation state after condensation. With these chemical and structural natures, the catalyst displays a remarkable electrocatalytic CO<sub>2</sub> reduction performance with an ethanol faradaic efficiency of 43.25 % at -1.0 V vs. RHE. At the same time, cobalt phthalocyanine just produced carbon monoxide and hydrogen. This is the first example of a cobalt phthalocyanine-based conjugated polymer that produces ethanol from CO<sub>2</sub> with a remarkable selectivity to the best of our knowledge.

## Enhancing Electrocatalytic Performance via Curvature-Tuned Hollow N-Doped Mesoporous Carbon with Embedded Co Nanoparticles for Oxygen Reduction Reaction

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Increasing catalytic performance is highly dependent on the rational design of the spatial structure of electrocatalysts, resulting from exposing the active sites, accelerating the rate of charge/mass transfer, and confining the reactants. Here we elaborately fabricate the Co nanoparticle embedded in the overhang-eave-like hollow N-doped mesoporous carbon (Co@EMPC) via tuning the stress by tuning the thickness of the mesoporous poly-dopamine (mPDA) for the first time. Benefiting from the abundant short mesoporous channels of the unique porous structure and unique electronic properties by heterojunction structures between metal and carbon, the as-prepared Co@EMPC possesses more accessible active sites and enhanced mass/charge transfer rate. These features contribute to remarkable performance for oxygen reduction reaction with a half-wave potential of 0.874 V vs RHE and superior durability in alkaline media. This study provided a new vision to improve the oxygen reduction reaction using eave-like hollow nanoreactor.



## When Single Atom Meet Nanoparticles/Nanoclusters for Oxygen Reduction

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Catalysts containing both single atoms and nanoparticles (NPs)/nanoclusters (NCs) have gradually been reported in recent years. These catalysts have the potential to combine the respective advantages of single-atom catalysts (SASCs) and nanocatalysts and make up for the respective limitations of each other. Meanwhile, the multiple active sites in the catalytic center may render them versatile binding modes toward adsorbates. Herein, we will report our works on nano-single-atom catalysts (NSACs) for oxygen reduction reaction (ORR). Specifically, the mechanism and origin of synergistic effects between NPs/ NC and related modulation methods are illustrated and summarized. Subsequently, we highlight the two categories of NSACs, nano-enhanced single-atom catalysts and single-atom-supported catalysts on the electronic structures, catalytic properties and functional mechanisms. We end by outlining strategies on how to fabricate NSACs. Finally, the future challenges and opportunities concerning the improvement of NSACs are outlined, which are essential to make such electrocatalysts viable for ORR.

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## Plasmon-driven Extra-high MOR Performance of Pd@Pt@Au Three-layer Core-shell Mesoporous Nanoparticles with Ex-situ Gold Positioning Enhancement

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Electrocatalysis is a pivotal field of research that holds tremendous promise for advancing renewable energy technologies and mitigating environmental challenges. The integration of mesoporous metal structures has emerged as a viable strategy to augment the catalytic activity and stability of bimetallic nanoparticles. The incorporation of gold into bimetallic mesoporous core-shell structures introduces several key changes such as modification the surface composition, leading to synergistic effects between the three metals, resulting in the formation of a surface plasmon resonance (SPR) band and enhancing light absorption and photothermal conversion efficiency.

In this study, our focus was on investigating the influence of gold deposition on the mesoporous structure of Pd-Pt in plasmon-enhanced photo-electrocatalysis. We proved that the addition of Au would greatly enhance the electrocatalytic activity, especially in the context of photo-electrocatalysis. Our results demonstrate that the precise control of the location and size of gold nanoparticles within the core-shell structure is crucial in designing highly efficient and selective plasmonic catalysts for renewable energy conversion and environmental remediation. Furthermore, the location of gold nanoparticles relative to the Pd-Pt mesoporous structure significantly impacts the catalytic performance.

These findings pave the way for the rational design and optimization of plasmonic catalysts, offering tailored properties for specific reactions and highlighting the importance of mesoporous metal structures in enhancing the overall catalytic performance of bimetallic nanoparticles. This research contributes to the growing body of knowledge in the field of electrocatalysis and presents new avenues for sustainable energy and environmental applications.

## Mesoporous Nanostructures for Exosome Profiling: A New Approach to Disease Diagnosis

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Tumour-derived exosomes have emerged as promising cancer biomarkers due to their distinctive composition and functions. However, research involving exosomes remains primarily confined to laboratory settings due to the intricate nature of specific isolation and sensitive quantification processes. Herein, we present a simple method for direct isolation and subsequent detection of a specific population of exosomes using a nanoarchitected superparamagnetic material with multifunctional properties, namely, iron oxide nanorods (IONR). To begin, the IONR is functionalized with a specific placental marker, anti-placenta alkaline phosphatase (anti-PLAP), for the isolation and detection of exosomes secreted from placental cells within the patient's plasma. This method enabled the sensitive detection of  $10^3$  exosomes per  $\mu\text{L}$  with a relative standard deviation (% RSD) of  $<5.5\%$  in both cancer cell lines and a small cohort of plasma samples ( $n = 10$ ) collected from patients with high-grade serous ovarian carcinoma (HGSOC). We believe that our approach could potentially represent an effective bioassay for the quantification of HGSOC-specific exosomes in clinical samples.

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## Hierarchically Porous Carbon Heterostructures from 2D Graphene Oxide with Enhanced Electrochemical Performance and Restacking Prevention

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Two-dimensional (2D) sheet-like materials benefit from high surface area and packing efficiency. However, the tendency of 2D materials to restack upon electrochemical cycling essentially blocks the passage of electrolyte ions into and out of the interlayer spaces between the sheets where various electrochemical processes need to be carried out. Incorporating micro-, meso-, and macroporosity into one hierarchically

porous and high-aspect ratio material may allow for increased rates of mass diffusion while maximizing the proportion of electrochemically accessible surface area and inhibiting the negative effects of restacking. Here, we report the synthesis of a hierarchically porous carbon heterostructure obtained via the growth of ZIF-8 and soft-templated polydopamine over the surfaces of graphene oxide, followed by carbonization. This heterostructured carbon inherits the high aspect ratio of the 2D GO template and the high electrochemically accessible surface area of the MOF-polymer porous system. This heterostructure demonstrated outstanding EDLC performance with a maximum capacitance value of  $343 \text{ F}\cdot\text{g}^{-1}$  at  $1 \text{ A}\cdot\text{g}^{-1}$ .

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## Temperature-Controlled Crystallization Technique for Enhanced Metastable CuTe<sub>2</sub> Thin Films for Optoelectronic Applications

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Binary metastable semiconductor materials represent a promising avenue in the realm of optoelectronics, offering diverse applications, including photovoltaics, tunable photosensors, and detectors.<sup>1,2</sup> However, the exploitation of their remarkable properties for practical implementations often needs to be addressed, stemming from their inherent thermodynamic instability.<sup>3</sup> This study presents a novel approach that merges temperature-controlled crystallisation<sup>4,5</sup> with electrochemical deposition, yielding metastable CuTe<sub>2</sub> thin films capable of robust operation under ambient conditions. The investigation involved a comprehensive series of *in situ* heating and cooling cycles, spanning the temperature range from room temperature to 200°C, followed by rigorous spectroscopic, morphological, and compositional analyses. Utilising techniques such as UV-Vis. spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), we delved into the intricate details of the CuTe<sub>2</sub> thin films' behaviour. Notably, our findings indicate a pivotal role played by the seeding electrodes in realising the metastable phase within the CuTe<sub>2</sub> films. Upon closer examination, CuTe<sub>2</sub> films deposited onto aluminium (Al) electrodes exhibited superior crystallinity and exceptional long-term stability, eclipsing those grown on traditional gold (Au) substrates. The XRD data of CuTe<sub>2</sub> films deposited on Al electrodes revealed a distinctively sharp peak following post-thermal annealing, signifying a substantial enlargement of crystal domain sizes. This remarkable enhancement contributes to the attainment of the metastable phase in CuTe<sub>2</sub>, resulting in a visible to near-infrared (NIR) active material boasting a band gap of 1.67 eV. Furthermore, our method demonstrated an elevated photoresponsivity across a range of illumination conditions, underscoring its potential for optoelectronic applications.

In summary, our study introduces a pioneering technique that harnesses temperature-controlled crystallisation in conjunction with electrochemical deposition to engineer metastable CuTe<sub>2</sub> thin films of exceptional quality and stability without the need for high temperature and pressure. The insight gained from this research holds promising potential in the field of optoelectronics by enabling the realisation of efficient photovoltaic devices, versatile photosensors, and high-performance NIR detectors, ultimately contributing to the evolution of sustainable and innovative energy technologies. The accrued insights hold far-reaching potential for catalysing advancements within optoelectronics, ushering in an era of efficacious

photovoltaic devices, adaptable photosensors, and high- performance detectors. This endeavour contributes substantively to the evolution of sustainable and avant-garde energy technologies, bridging the divide between theoretical potential and practical realisation.

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## Session: ITB-UQ Special Session (Sponsored by UQ Global Engagement)

### Modification of Metal Organic Frameworks (MOFs) for Electrochemical and Optical Biosensor

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Metal organic frameworks (MOFs) are one class of porous materials that gained significant interest in sensing applications because of their unique properties including high surface area, abundance active sites, tunable pore, and tunable surface chemistry. In addition, sensing properties can be significantly improved by controlling morphology of MOFs which basically induce defect on their surface. The function of the defect is to open active sites, enabling surface modification, and increase catalytic activity. For example, one dimensional HKUST-1 was prepared using a simple co-precipitation method with the presence of thiethanolamine as a pH modulator and structure directing agent at the same time. Using electrochemical techniques, 1D HKUST-1 modified glassy carbon electrode displays limit of detection of 12 pg/mL in detecting NS1 Dengue virus antigen. The amorphous HKUST-1 was also successfully prepared using the similar technique. The limit of detection can be lowered to 1.64 pg/mL. In addition, modification of HKUST-1 was also achieved by incorporating different metal forming bimetal HKUST-1. For example, cobalt was incorporated into HKUST-1 to improve the sensing performance toward Dengue virus. With the copper to cobalt ratio of 2:1, the limit of detection 0.17 pg/mL. Aside from Dengue virus, amorphous HKUST-1 was applied as Hepatitis B sensor. In this case anti-HbsAg was used as a bioreceptor. The immunosensor has detection limit down to 0.87 pg/mL and has high potential for early detection of Hepatitis B. Another kind of MOF was also utilized in optical biosensor such as UiO-66. The UiO-66 modified gold chip can detect the presence of HER2 which is biomarker for breast cancer anti RBD which is protein in Sars-cov-2, with detection limit of 5.92 ng/mL and 0.18 ng/mL respectively. These results show the high potential of MOFs in biosensor application.

### Micellar Solutions Approach of Mesoporous Pd and PdCu Nanoarchitectures for Electrocatalytic Applications

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Noble metals are important materials that increase the efficiency of chemical reactions in organic chemistry and electrocatalysis. Palladium (Pd) in particular is an essential component in various reactions including the electrocatalytic oxidation of hydrogen and other small molecules, and the electrocatalytic reduction of oxygen. Controlling the shapes, compositions, and sizes of Pd nanoparticles enables beneficial tuning of their properties and interfacial surface effects for suitable applications. In general, ultra-small Pd nanoparticles (2~10 nm) are most often utilized as catalysts in industry. However, they tend to suffer performance degradation because their chemical and thermal stabilities are very poor, and they easily undergo structural transformations under reaction conditions. Recently, researchers have been exploring more cost-effective electrocatalysts based on alloys of Pd metal with non-noble metals including copper, Cu. The presence of the second element can increase the electrocatalytic activity and stability of Pd catalysts. To further improve the catalytic properties of Pd-based materials, it is important to introduce novel nanostructures. Among previously reported nanostructures, mesoporous architectures are quite promising due to their high specific surface areas and exposed catalytically active sites. Herein, the development of Pd-based nanostructures and mesoporous materials by combining shape- and structure-directing agents with wet-chemical and electrochemical synthetic approaches will be presented. The approach establishes a platform for the facile synthesis of mesoporous Pd-based nanoparticles and films, which can be extended to other metallic nanostructures for a wide range of applications.

## Hollow Zinc-oxide Microsphere–multiwalled Carbon Nanotube Composites for Selective Detection of Sulfur-dioxide

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This work report on a facile anthocyanin-assisted solvothermal method for formation of three dimensional zinc oxide (ZnO) hollow sphere and its modifications with multi-walled carbon nanotubes (MWCNTs) as a sensitive layer for sulfur dioxide (SO<sub>2</sub>) detection. The anthocyanin was extracted from local Indonesian black rice. The as prepared ZnO structurally has wurzite hexagonal crystal structure even before calcination process, and it has sphere like morphology with the cavity observed inside the sphere. The sphere of ZnO is arranged by nanoparticles with the size of around 10 nm. Furthermore, the presence of MWCNT could destroy the hollow sphere structure of ZnO by penetrating into the inside part of the sphere, and it was observed that some ZnO nanoparticles grew on the MWCNT surface. As SO<sub>2</sub> sensor material, ZnO-MWCNT composite 15:1 displays a high response of 156 to 70 ppm of SO<sub>2</sub> at temperature of 300 °C. That value is more than three times higher than the response of pure ZnO hollow sphere at the same temperature. The high performance of composite ZnO-MWCNT 15-1 is also shown by its good selectivity to 50 ppm

of SO<sub>2</sub> with the response value is more than three times higher than the responses to other tested gases. We also observed that the sensing behavior of the composite is depend on the concentration of MWCNT. N-type behavior is observed on the composite of 15-1 and 10-1, while p-type behavior is observed on the composite of 5-1. This switching behavior indicate the major contribution of p-type MWCNT to electronic and sensor properties of composite.

## Sodium Dodecyl Sulfate Assisted Synthesis of NiO Microflowers-like on Nickel Foam as An Advanced Supercapacitor Electrode

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The transition metal oxide NiO is a promising candidate for future supercapacitor devices due to its unique electrochemical activity and low cost. Nevertheless, the weak interaction between NiO and conductive substrates results in poor mechanical strength. Herein, the NiO microflowers-like has been prepared on nickel foam via hydrothermal and calcination process. The NiO microflowers-like has a specific surface area of 10.47 m<sup>2</sup> g<sup>-1</sup> and an average pore width of 21.91 nm. In the CV curve, NiO microflowers-like shows a very clear redox peak. The two broad peaks depict the energy storage mechanism via the reversible Ni<sup>2+</sup>/Ni<sup>3+</sup> redox reaction. The anodic and cathodic peaks correspond to the adsorption and desorption of OH<sup>-</sup> ions that occur on the NiO microflowers-like electrode surface. Furthermore, based on the Power law ( $i = av^b$ ), the NiO microflowers-like electrode demonstrates the battery-type category. As a supercapacitor electrode, the NiO microflowers-like shows an areal capacity of 393 mC cm<sup>-2</sup> at 0.5 mA cm<sup>-2</sup>.

**Keywords:** Sodium Dodecyl Sulfate, NiO microflowers-like, supercapacitor electrode.

## Designing Aptasensor Based on Surface Plasmon Resonance for COVID-19 RNA Detection

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Coronavirus or COVID-19 is a virus from the Coronaviridae family that has been epidemic throughout the world since the end of 2019. The virus spreads ten times faster through human interaction than SARS-CoV. RNA sequence of COVID-19 has 79,5% similarity with SARS-CoV. Fast and specific detection of COVID-19 is needed so that patient detection can be done quickly and accurately. One method that can be developed as a COVID-19 biosensor is aptamers-based biosensors. Aptamers are artificial oligonucleic acids that can specifically bind to target molecules. Aptamers are easily chemically modifiable for increasing stability and reducing toxicity. They show a comparable affinity for the target virus and better thermal stability than monoclonal antibodies. Those advantages make aptamers promising candidates in diagnostic and detection applications. The goal of this research was to use Aptamer RNA as the specific recognition element in a portable surface plasmon resonance (SPR) biosensor for the detection of COVID-19 in humans. In this work, two aptamers were designed (APT-1 and APT-3) as a biorecognition for Covid-19 RNA detection. APT-1 COVID-19 was designed using the COVID-19 sequence from GISAID using the *in silico* method. End of 3' APT-1 modified with dithiol. Then, the aptamer was immobilized on the gold nanoparticle sensor chip via Cysteine-dithiol binding. The RNA solution that had been extracted from swab samples, was diluted ten times before being used as a sample. The immobilized APT-1 captured COVID-19 in RNA solution, causing an increase in refractive index (r.u). APT-1 was found to bind RNA virus of COVID-19 better than APT3 where the positive sample of COVID-19 has refractive index (r.u) between 1 r.u - 3 r.u for various Ct values. Whereas the negative sample response was only 0,5 ru. From the calculation result obtained LOD for the chip biosensor with APT-1 is 1.2805 uM and the chip biosensor with APT-3 is 1.2479 uM.

## One Pot Synthesis Process of Hollow Two-dimensional Bimetallic Metal-Organic Framework Hexagonal Nanoplates for Ammonia Sensing

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A lot of interest has been paid to two-dimensional metal-organic framework (2D MOF) nanostructures because of their extreme thinness, high surface-to-volume ratio, and highly exposed active sites. This study describes the production of hollow bimetallic nickel-cobalt benzene tricarboxylic acid (Ni-Co BTC) hexagonal nanoplates without the need of templates or etching, with the aid of polyvinylpyrrolidone (PVP). The adsorbed PVP molecules can provide depletion forces between the nanoplates to prevent their aggregation and limit the vertical growth of MOF layers, which can encourage the production of thin hexagonal nanoplates. In comparison to non-hollow Ni-Co BTC nanoplates, Ni-BTC nanobelts, and Co-BTC microrods, respectively, the hollow Ni-Co BTC hexagonal nanoplates show 1.6, 3.8, and 7.5 times higher sensitivity to NH<sub>3</sub>. Additionally, they exhibit remarkable stability with just a very slight drop of 2.86% over a period of 6 months and good selectivity to NH<sub>3</sub> in the presence of other interfering substances and water. The hollow bimetallic Ni-Co BTC nanoplates improved sensitivity and selectivity are related to the presence of carboxyl and hydroxyl groups, which can encourage hydrogen bonding with NH<sub>3</sub> molecules.

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## Template-free Method to Enlarge the Porosity of Metal-Organic Framework Derived Carbons for Supercapacitor Electrodes

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Metal-organic frameworks (MOFs) have drawn great interests as both carbon sources and self-templates for creating carbon materials with intrinsic porosity, tuneable chemical and physical properties and high surface area.<sup>1,2</sup> Hard or soft template methods have been primarily used in the preparation of hierarchical porous carbons.<sup>3</sup> The template-based approaches, however, require uniform combination of the carbon sources with templates and post-synthetic template removal, making the fabrication procedures costly and complex. Herein, we demonstrate a facile template-free etching strategy for enlarging the micropores in bimetallic zeolitic imidazolate framework (ZIF) particles into mesopores at room temperature. Hierarchical porous bimetallic ZIF particles (etched  $Zn_{33}Co_{67}$ -ZIF) exhibiting both micropores and mesopores have been successfully prepared while maintaining the framework integrity using the ethylene glycol-assisted aqueous etching method. After pyrolysis, the etched  $Zn_{33}Co_{67}$ -ZIF particles are transformed into cobalt- and nitrogen-doped hierarchical porous carbon (i.e., etched  $Zn_{33}Co_{67}$ -C) particles with increased mesoporosity. The etched bimetallic carbon (etched  $Zn_{33}Co_{67}$ -C) displays 1.6- and 14.8- times higher specific capacitance at a high scan rate of  $100\text{ mV s}^{-1}$  than unetched bimetallic carbon ( $Zn_{33}Co_{67}$ -C) and Zn-only carbon (Zn-C), respectively as electrochemical double layer supercapacitor electrode materials. Additionally, the etched  $Zn_{33}Co_{67}$ -C exhibits good electrochemical stability after 5,000 cycles. The presented ethylene glycol-assisted aqueous etching process provides a useful method for enlarging the porosity of MOFs, and their corresponding porous carbon materials and improve their supercapacitor performance.

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## Synergistic Mesoporous Bimetallic Gold-Silver Nanoparticles: Synthesis, Structure, and Superior Electrocatalytic Activity

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Owing to the large surface area and high degree of accessible pores with good stability, nontoxicity, and good resistance to poisoning effects during the electrochemical reaction, mesoporous gold (Au) structures with surface dominated by active low-coordinated atoms have significant enhancement as an



electrode in the catalytic reaction of small organic molecules<sup>1</sup>. Modifying the composition by introducing such cheap metals like silver (Ag) to prepare bimetallic Au-based catalyst is expected to improve the surface adsorption/desorption properties hence increasing the catalytic activity. However, the high mobility and oxidation potential of Au precursors make it challenging to create Au-based NPs with pores of sufficient size to maximize reactant-catalyst interaction. In this study, we report a novel and straightforward one-pot chemical reduction method to synthesize mesoporous AuAg nanoparticles with a large mesopore size (>10 nm) and a well-defined structure. The synthesis involves the use of L-cysteine as a ligand to form thiolate-metal(I) complexes and co-reduction of the metal precursors around the sacrificial templates of polymeric micelles. The resulting nanoparticles exhibit a highly uniform size and possess a well-ordered mesoporous structure. Structural measurements confirm the formation of an alloy system containing Au and Ag without any separate phases. By changing the initial precursor composition, it is possible to control the Au:Ag ratios in the final products. The electrocatalytic activity of mesoporous AuAg nanoparticles in the electrooxidation of small molecules surpasses that of mesoporous Au nanoparticles, which is attributed to the synergistic effect arising from both the alterations in the electronic structure and the benefits offered by the porous architecture. Our synthetic approach provides a promising avenue for developing efficient and cost-effective mesoporous Au-based nanoparticles for a diverse range of applications.

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**Day 2 ABSTRACTS**

**September 28, 2023**

## Session: JST-ERATO Special Session

### Extraordinary Properties of Mesoporous Bi<sub>2</sub>Se<sub>3</sub> Film

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Nanoarchitectonics, the engineering of nanomaterials' structure at the atomic/molecular level, aims to comprehend and develop strategies for designing and functionalizing materials. The control of the nanostructure of metal chalcogenides, which possess unique electronic structures, can enhance their properties or introduce new attractive characteristics. Among metal chalcogenides, Bi<sub>2</sub>Se<sub>3</sub> has garnered significant attention as a promising material for optoelectronics and thermoelectric devices due to its relatively simple electronic structure and n-type characteristics. In particular, Bi<sub>2</sub>Se<sub>3</sub> exhibits a topological insulator's behavior within a specific crystal structure (*i.e.*, rhombohedral), wherein the bulk structure behaves as an insulator, while the surface displays metallic characteristics. This presentation is focused on the incorporation of a uniform pore structure throughout the Bi<sub>2</sub>Se<sub>3</sub> film and the distinct surface conduction properties resulting from an increased surface area. The study explores the control of surface area by manipulating pore size and its impact on surface conduction properties.

## Nanoarchitected Porous Carbons to Achieve Controlled and Open Porosity

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A variety of carbon materials has been synthesized and utilized throughout the human history beginning from the ancient use of porous charcoals for medical purposes. With the advance of science and nanotechnology, the properties of carbon materials are now better understood, and more precise synthesis of novel carbon materials has become possible. Among different types of carbon materials, porous carbons are widely studied because of their high surface area, electrical conductivity, outstanding chemical/mechanical stability, and easy modification of surface chemistry. Despite such benefits, it is still challenging to achieve a high level of control over the porosity mainly due to their complicated synthetic routes. Besides, an in-depth understanding of the effect of each class of nanopore (micro-/meso-/macropore) is necessary to strategically design and synthesize porous carbon materials that are suitable for specific electrochemical applications. In this presentation, several types of nanoarchitected carbon precursors (e.g., biomasses, metal-organic frameworks, and polymers) and their carbons will be introduced to provide a further understanding of the effect of porous structure in the context of electrochemical applications. The results indicate that it is important for the porous carbons to have their nanopores well-opened to the surrounding environment while having a broad distribution of nanopore sizes (*i.e.*, hierarchical porosity). It is also demonstrated that a significant portion of the high surface area of porous carbons can become inaccessible/redundant, especially in electrochemical applications, without a careful consideration of the openness and the hierarchy of nanopores in the synthesis. This presentation will eventually further emphasize the importance of nanoarchitectonics in trying to bring the full potential of porous carbons.

## Mesoporous Architectures of Metallic Amorphous Alloys

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Mesoporous metallic materials with high surface areas, adjustable pore structures, and efficient mass/electron transportation processes are important components in the field of nanomaterials. However, traditional mesoporous metals are mostly based on crystalline alloys, primarily composed of precious metals. In contrast to crystalline materials, amorphous alloys exhibit highly uncoordinated metal bonds, uniform active sites, and disordered atomic arrangements, garnering significant attention. Introducing mesoporous structures into amorphous alloys is a challenging and arduous task, especially for non-precious metal amorphous alloys. In this presentation, we will primarily focus on the characteristics of amorphous alloys and the mechanisms behind mesoporous structure formation within them. Moreover, through precise control of synthesis methods, we have achieved compositional diversity and dimensional expansion of mesoporous amorphous alloys. The structure-performance relationships of these materials in various applications were also introduced.

## Promoting Electrochemical Energy Storage Performance of Nanosheets by Developing Novel 2D Nanoarchitected Hybrid Materials

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The fast-growing interest in two-dimensional (2D) nanomaterials is undermined by their natural restacking tendency, which severely limits their practical application. The hybridization of 2D nanosheets with other low-dimensional materials, such as nanotubes and nanoparticles, can generate additional channels for ion transportation within the interlayer space. Recently, a new class of 2D porous heterostructures, in which an ultrathin 2D material is sandwiched between two mesoporous monolayers assembled on either side, has introduced a new paradigm to the field of 2D materials. The novel porous heterostructure produces unique characteristics that are not found in other 2D material hybrids and composites, such as the high exposure of their surface area to electrolyte and their well-defined pores for charge transfer. Control over the geometry of mesoporous layers (e.g., pore size and orientation and layer thickness) can be achieved by selecting different structure-directing agents (e.g., type and molecular weight) and by controlling the assembly conditions to satisfy design requirements. The efficacy and versatility of this concept is demonstrated by the substantially enhanced capacities, improved rate capabilities, and longer life stabilities of energy storage devices, including supercapacitors, Li-S batteries, Li-ion batteries, and Na-ion batteries.

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## Flexible Mesoporous Gold Sensor for Biosensing and Physiological Neural Recording

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The implantable biomedical devices provide powerful tools for biomedical applications, especially for *in-vivo* diagnostics, physiological neural recording, and modulations.<sup>1</sup> The commercially available implantable devices encapsulated in thick ceramic housing for electronics present potential risks to the users and limit functional options due to mechanical mismatch between implanted components and soft tissue.<sup>2</sup> In contrast, flexible electronic platforms offer exciting opportunities for integrating electronics seamlessly into tissues. Furthermore, the implantable device should have a low impedance at the electronic-tissue interface so it can detect relatively low biopotentials, typically within the range of a few microvolts.<sup>3</sup> To address these issues, we present a novel engineering approach that combines top-down and bottom-up methods to selectively synthesize flexible mesoporous metallic gold films as electrodes for biosensing and bioimplant applications. The porous network of gold can significantly boost the overall performance of implantable devices because of the significantly increased surface area, high absorption spectrum for optoelectronics, excellent electrochemical properties for sensing, and the capability of loading and releasing biomolecules. The mesoporous gold architectures developed on a thin and soft polymeric substrate provide excellent

mechanical flexibility and stable electrical characteristics capable of sustaining multiple bending cycles. The large surface areas formed within the mesoporous network allow for high current density transfer in standard electrolytes, highly suitable for biological sensing applications as demonstrated in glucose sensors with an excellent detection limit of 1.95  $\mu\text{M}$  and high sensitivity of 6.1  $\text{mA cm}^{-2}\mu\text{M}^{-1}$ . The low impedance of less than 1  $\text{k}\Omega$  at 1 kHz in the as-synthesized mesoporous electrodes, along with their mechanical flexibility and durability, offer peripheral nerve recording functionalities that are successfully demonstrated *in vivo*.

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## Piezoelectric Properties in Nanoporous Thin Film

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In the field of conductive, dielectric, and magnetic materials, the development of stable functional materials is strongly required. Especially, it is difficult to design dielectric crystals which can control electric properties unlike the conductive and magnetic materials. The fusion of different components has potential to create new possibilities.

The creation of porous structure in the dielectric materials has also shown great improvement. Barium titanate ( $\text{BaTiO}_3$ ; BTO) family is one of the environmentally friendly lead-free piezoelectric materials to replace lead zirconate and lead titanate,  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT). Especially,  $\text{Ba}_{0.85}\text{Ca}_{0.15}(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$  (BCZT) film has attracted attention as a promising piezoelectric material. However, the value of piezoelectric strain constant  $d_{33}$  and electromechanical coupling factor  $k_{33}$  in BTO is still far behind that of its commercially available Pb-based counterparts [1]. In our study, we have found the giant  $d_{33}$  in nanoporous BCZT film. Comparing to non-doped BTO, non-porous BCZT and PZT, one of the typical piezoelectricity, the value of  $d_{33}$  for nanoporous BCZT is much larger than that for them [2].

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## Analysis of Pathological Manifestations in Reservoirs of Reinforced Concrete in the City of Porto Alegre in Buildings with Age Over 20 Years

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Concrete reservoirs can be considered obsolete structures in buildings currently, but they are still problem in older condominiums. The advent of new materials, recent constructions have opted for lighter, less-maintenance material reservoirs. There are many buildings with reservoirs concrete. Concrete reservoirs are subject degradation mechanisms like radiation, rainfall, thermal variations, biological and chemical attacks and internal stress. This make it necessary to periodic inspections and preventive maintenance to prevent the emergence of anomalies in the structure, w compromising its performance, and consequently its durability.

This study was to analyze the pathological manifestations, with significant damage to reinforced concrete reservoirs in the Porto Alegre city, in buildings older than 20 years, detecting their origin and causes, as well as, through research for new techniques. and new materials, recommend maintenance.

**Keywords:** Concrete reservoirs. Pathological manifestations. Degradation. Periodic inspection. Preventive maintenance.

## Sandwich-structured $MSn_x$ -rGO-SnO<sub>2</sub> Nanocomposites Modified by Intermetallic Compounds for Enhancing Sub-ppm H<sub>2</sub> Detection

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SnO<sub>2</sub> nanoparticles were grown on the surface of reduced graphene oxide (rGO) via a simple reflux reaction, resulting in the formation of rGO-SnO<sub>2</sub> nanocomposites with excellent hydrogen (H<sub>2</sub>) sensing performance. Noble metal sensitizers, known for their electronic and chemical sensitization effects, have been shown to significantly enhance the sensing performance of metal oxide semiconductor (MOS) based gas sensors. In recent years, intermetallic compounds have gained significant attention in catalysis research due to their tunable electronic structure, excellent stability, and low cost. Especially, intermetallic compounds have demonstrated exceptional catalytic performance. Based on the theoretical basis of the above two aspects, it is hypothesized that intermetallic compounds will offer high sensitization performance in MOS gas sensing. Herein, an in-situ synthetic approach to produce a series of intermetallic sensitizers consisting of three binary M-Sn (M: Au, Pt, Pd) intermetallic compounds were reported. All three intermetallic compounds significantly enhanced the H<sub>2</sub> sensing performance of rGO-SnO<sub>2</sub> nanocomposites, with Pd<sub>3</sub>Sn<sub>2</sub> exhibiting the most potent sensitizing effect. The 2.0% Pd<sub>3</sub>Sn<sub>2</sub>-rGO-SnO<sub>2</sub> nanocomposites with sandwich structure showed a significant decrease in the optimal operating temperature of rGO-SnO<sub>2</sub> nanocomposites in response to H<sub>2</sub> from 225 °C to 90 °C, and its sensor response to 500 ppm H<sub>2</sub> was 250.9, which was 125 times higher than that of rGO-SnO<sub>2</sub> nanocomposites.

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## Effect of Saltwater Mixing and Curing on the Compressive Strength of Cement Mortar with Blast Furnace Slag

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Global concrete production consumes about 18% of the world's annual industrial water consumption. By 2050, 75% of concrete water demand may occur in areas facing water stress area [1]. In addition, the production of cement releases a large amount of carbon dioxide, which seriously impacts the environment [2, 3]. How to use blast furnace slag and other industrial by-products instead of cement to produce concrete and reduce the use of cement has become an important issue [4, 5]. Considering the increasing shortage of freshwater in the world, the amount of seawater is much more significant than that of freshwater, which can provide stable mixing water for producing concrete. Therefore, this study investigates the effect of saltwater mixing and curing on the compressive strength of cement mortar with blast furnace slag.

In this study, blast furnace slag was used to replace 30% cement (weight replacement), freshwater, and saltwater (half, the same, and two times the concentration of seawater) used to produce cement mortar. Then these four kinds of mixing water were used to cure the mortar till the test ages (7 days and 28 days). The test results show that, at the age of 7 days, the compressive strength of mortar with blast furnace slag mixed with the saltwater (the same seawater concentration) and cured by the saltwater (half time the seawater concentration) is the highest (78MPa). The control mortar specimen mixed and cured with freshwater has the lowest compressive strength (36.2MPa). At 28 days, the compressive strength of mortar with blast furnace slag mixed with the saltwater (two times the seawater concentration) and cured by the saltwater (half time the seawater concentration) is the highest (90.2MPa). The strength of the control mortar is 53.0MPa under the same curing conditions, which is still relatively low. It can be seen from this that the mixing and curing of saltwater are helpful to the improvement of the compressive strength of cement mortar. The cement mortar with 30% blast furnace slag, mixed with freshwater and cured with saltwater twice the seawater concentration, has a higher strength at 28 days.

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## Nanocomposites Thin Films Based on Octahedral Metal Atom Clusters

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This presentation will summarise our recent works on the synthesis of functional nanocomposites thin films based on metal atom clusters by a chemical solution deposition (CSD) processes [1-11]. CSD processing of inorganic nanocolloidal solutions is generally acknowledged to be highly flexible in terms of precursor composition, targeted substrate and procedures (dip-spin-bare coating, spray coating, EPD...) in ambient pressures, and thus can be faster and less expensive than physical-based deposition routes while providing materials with matching or even superior properties. In this study, several octahedral atom clusters were characterised and used to prepare highly transparent thin films in the visible. Various coloured and transparent films were successfully fabricated on ITO glass substrates. In addition, transparent films with prominent photoactive or antibacterial properties were obtained by using specific  $\text{Mo}_6$  clusters whereas UV and NIR filters were realised by using  $\text{Ta}_6$  and  $\text{Nb}_6$  clusters. The CSD processes appear as a performant strategy to fabricate highly transparent and coloured nanocomposite thin films for optical, biological and energy applications.

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## Biomass-derived Functional Nanocomposites for Practical Applications

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Nowadays, the widespread use of plastics has brought convenience to human life, but it has become a serious pollutant around the world. Indeed, 8.5 million tons of plastic waste is generated every year, causing critical damage to organisms and the environment. Natural biomass, which is abundant in nature, is an alternative to solve this problem due to its cost-effectiveness, sustainability, and biodegradability. Here, we describe functional nanocomposites that exhibited electrical conductivity by incorporating a conductive material into biomass. These functional nanocomposites can be used in 'green' electronics such as circuits, sensors, and energy storage systems. We successfully fabricated transparent and flexible silver nanowires (AgNWs)/cellulose nanofiber (CNF) microelectrodes with 500  $\mu\text{m}$  of pattern size by photolithography patterning and vacuum-assisted microcontact printing. The resulting AgNWs/CNF nanopaper showed an optical transparency of 82% at 550 nm and a sheet resistance of 54  $\Omega \text{ sq}^{-1}$  when the surface density of AgNWs was as low as 12.9  $\mu\text{g cm}^{-2}$ . Furthermore, no significant change in electrical resistance was observed after 500 cycles of 80% bending strain, indicating its excellent bending stability. Next, we constructed hydrogel-based flexible microelectrodes based on AgNWs and agarose for use as a pressure sensor. The AgNWs/agarose composite hydrogel exhibited high conductivity ( $8.40 \times 10^3 \text{ S cm}^{-1}$ ) with low sheet resistance ( $7.51 \pm 1.11 \Omega \text{ sq}^{-1}$ ), excellent bending durability (increases in resistance of only  $\sim 3$  and  $\sim 13\%$  after 40 and 160 bending cycles, respectively), and good stability in wet conditions (an increase in resistance of only  $\sim 6\%$  after 4 h). The pressure-responsive sensor, in the form of a sandwich-type of two AgNW electrodes on hydrogel, was highly responsive to low pressure sensing range ( $< 2.5 \text{ kPa}$ ). We have fabricated a self-standing, highly flexible, and conductive poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS)/CNF composite film. The resultant composite film showed competitive electrical conductivity ( $22.6 \text{ S cm}^{-1}$ ) and

excellent bending stability without disconnection of the conductive area during 100 times at an angle of 180°. Furthermore, post-treatment with organic solvent led to the removal of residual PSS, resulting in a significant increase in electrical conductivity. The electrical conductivity of PEDOT:PSS/CNF nanocomposite paper post-treated with dimethyl sulfoxide (DMSO) and ethylene glycol (EG) increased from 1.05 S cm<sup>-1</sup> to 123.37 S cm<sup>-1</sup> and 106.6 S cm<sup>-1</sup>, respectively. In addition, the excellent capacitance retention of the post-treated nanocomposite paper was confirmed, indicating well-dispersed PEDOT:PSS in a stable, porous CNF structure. Functional nanocomposites based on biomass and conductive materials have not been limited to 'green' electronics. We produced a PEDOT:PSS/agarose composite hydrogel that was capable of stable coating on a variety of substrates and pre-programmed shapes. Due to the photothermal effect of PEDOT:PSS, the composite hydrogel exhibited a temperature increase of up to 50 °C when exposed to near-infrared (NIR) light, which induced photothermolysis killing of pathogenic bacteria on the hydrogel surface. It was demonstrated that all *E. coli* were eliminated within 2 minutes of NIR irradiation. The self-healing ability of the composite hydrogel was demonstrated by continuous damage and healing processes under NIR irradiation.

### Reduced Ice Adhesion using Amphiphilic Poly (Ionic Liquid)-based Surfaces

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Ice build-up on solid surfaces pose a serious safety hazard and can lead to significant economic losses for a range of industries [1]. One solution to this problem is development of icephobic coatings. Amphiphilic icephobic coatings have been recently developed in which the combination of hydrophilicity and hydrophobicity could overcome the limits of hydrophobic coatings for reducing the ice adhesion strength [2]. Amphiphilic poly-(ionic liquid) (PIL) based surfaces have shown to be promising for anti-fogging / anti-frosting applications due to depression in the freezing point of water [3]. However, their anti-icing properties through lowering the ice adhesion strength have yet to be investigated.

This presentation will outline the development of well-controlled amphiphilic triblock copolymers comprised of a hydrophobic component coupled with PIL segments to create surfaces with low ice adhesion strength. The structure-property relationships of the resultant coatings by varying the content of the PIL segments, the counter-ion and the crosslinking density will also be presented.

Through delicate balance of amphiphilicity, one of the lowest values of ice adhesion strength in the field of amphiphilic anti-icing coatings is obtained, enabling the easy removal of ice from the surface by natural wind action. Characterization of the coatings in terms of surface features, wettability, hydration state, and elastic modulus have enabled elucidation of different de-icing mechanisms. This work offers a new approach for the exploration of PIL-based icephobic coatings for practical applications.

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### Catalytic Conversion of Pulegone to Thymol using a Novel Trimetallic (Al-B-Pd/Ac) Composite Material: A Perspective on Flavor and Food Control

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Pulegone, a monoterpene compound found in mint plants such as peppermint, spearmint, and pennyroyal, has been identified as a carcinogen causing hepatic carcinomas, pulmonary metaplasia, and other neoplasms upon oral administration in rodents. Consequently, in 2018, the US Food and Drug Administration banned the use of synthetic pulegone as a food additive. In this research, we synthesized novel tri-metallic catalysts (Al-B-Pd/AC) to selectively convert pulegone to thymol. The synthesized catalysts exhibited high activity in the selective reduction of pulegone to both menthone and thymol under mild reaction conditions. Specifically, the Al-B-Pd/AC catalyst, under optimal reaction conditions (70°C temperature, 30 minutes reaction time, and 10 psi hydrogen pressure), achieved >95% conversion of pulegone to thymol with approximately 100% selectivity. The synthesized catalysts demonstrated excellent thermal stability, as confirmed by TGA, and no leaching issues were observed during the reaction process. Subsequently, these catalysts were employed under their optimal reaction conditions to reduce pulegone content in essential oils containing pulegone, such as CIM-visisth and peppermint. This approach successfully achieved a reduction in pulegone percentage to less than 0.5%. Furthermore, the catalysts underwent thorough characterization using SEM, TEM, XPS, SA, and XRD analysis. The catalysts' high reusability and the utilization of low operating reaction conditions contribute significantly to the overall cost-effectiveness of the process and facilitate its seamless scalability to an industrial level.

**Keywords:** Catalytic transformation, Heterogeneous catalyst, Pulegone, Thymol.

## Session: Advanced Nanomaterials

### Self-assembly of Monodisperse Nanosheets

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Inorganic nanosheets are usually obtained by exfoliation of layered crystals and are known to form intriguing colloidal liquid crystals (LC) under a certain condition<sup>[1,2]</sup>. They have been applied for fabrication of anisotropic polymer composite materials<sup>[3]</sup>, structural color materials,<sup>[4,5]</sup> etc. However, large polydispersity in lateral size limited more precise design of the self-assembled structures and materials properties.

Here, we demonstrate that very unusual mesophases are reversibly formed by self-assembly of monodisperse titanate nanosheets that were synthesized by the bottom-up method<sup>[6]</sup>. Small angle X-ray scattering (SAXS) and transmission electron microscopy revealed the formation of one-dimensional long columns of stacked nanosheets. With the increase of nanosheet-nanosheet interaction, the columnar nematic LC phase appeared as confirmed by polarized microscopy and SAXS; this is the very first observation of such the LC phase in a nanosheet colloid. In some cases, the columns were further assembled into micrometer-scale fibrous bundles with well-defined supercrystalline structures. The formation and dissociation of these structures were reversible and controllable by several factors such as temperature. While monodisperse CdSe nanosheets have been reported as the only example to form similar long columnar structures under limited conditions,<sup>[7]</sup> the present system is distinguished by the widely controllable and reversible formation of various hierarchical superstructures and LC phases. The formation of these superstructures is rationalized by weak nanosheet-nanosheet attractions as well as by an entropic excluded volume effect.

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## Surfactant-assisted Synthesis of Mesoporous Metal Phosphonates and Unique Surface and Interior Properties

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A variety of potential applications have been reported so far through the design of periodic mesoporous organosilica (PMO) type materials. However, almost of the properties arising from the function of integral organic groups have been investigated inside their resultant hydrophobic mesopores. Here, I will mainly introduce my own achievements in the synthesis of analogous non-silica-based hybrid mesoporous materials. According to my original approach to control the reactivity of bisphosphonates to metal sources,<sup>1</sup> a number of interior organic groups, such as designable benzene and bulky biphenyl, have been integrated inside an aluminum phosphate like framework.<sup>1-3</sup> This initiative has also been extended to the preparation of a titanium phosphate like framework.<sup>3</sup> Surface property (hydrophilicity and hydrophobicity) was carefully evaluated through adsorption measurement of molecular H<sub>2</sub>O and contact angle measurement of cluster H<sub>2</sub>O. The H<sub>2</sub>O adsorption measurements indicated that the aluminum phosphonate-based framework was hydrophilic by the presence of AlO<sub>4</sub> units but fixed to be hydrophobic through the incorporation of bulky organic groups such as benzene and biphenyl. In contrast, the H<sub>2</sub>O contact angle measurements revealed that surface properties of mesoporous aluminum and titanium phosphonate films were hydrophilic even in the presence of bulky biphenyl group. Accordingly, it is rational to consider that molecular H<sub>2</sub>O (vapor, equilibrium) is sensitive to chemical composition as well as molecular-scale framework structure and cluster H<sub>2</sub>O (droplet, kinetic) is mainly interacted to surface hydroxyl (-OH) group. This insight is important for understanding an intrinsic interaction to materials by using H<sub>2</sub>O as molecule and droplet.

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## Rational Design of Single-phase Multi-metal Mesoporous Nanostructures for a Sustainable Future

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Ecofriendly electrochemical energy conversion devices require rationally designed electrocatalysts for their efficient operation. The recent developments in multi-metallic nanostructures, particularly high entropy alloy (HEA) with five or more elements uniformly distributed throughout the nanostructure, have opened a new avenue to explore the structure-property correlations. The synergy of multi-metals in HEAs creates numerous electroactive sites, enabling a near continuum of surface adsorption/desorption energies. Developing the single-phase HEA nanostructures is challenging due in part to the different surface energies of the metals— making HEA nanostructures that are mesoporous is even more difficult. However, the benefits of mesoporous HEA systems enable tunable metals with high surface areas, more exposed active sites, enhanced material utilization and better mass/charge transportation. Herein, we present a simple low-temperature colloidal method to create mesoporous HEA nanostructures. By carefully tuning the experimental conditions, we could tune the compositional space of the HEA and the concomitant multi-functional activities. Our methodology can be extended to design different combinations of HEA systems for targeted applications.

## Session: Energy and Environmental Materials

### Surface tension and viscosity measurement of molten materials using aerodynamic levitation technique

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For accurate modeling of the casting process, crystal growth, additive manufacturing, and so on, thermophysical properties of molten materials at high temperature are required. In the conventional thermophysical property measurement methods of the high-temperature melts, reactions between container and high-temperature molten materials disturb the high accuracy thermophysical property measurement of the molten materials. Containerless levitation techniques are powerful tools for measuring thermophysical properties of molten materials at high temperatures. The levitation techniques have large advantages for keeping liquids in a supercooled state and for maintaining the high-temperature state while maintaining the high purity due to the containerless environment. This makes it possible to precisely determine the temperature dependence of the thermophysical properties of molten materials over a wide temperature range. Aerodynamic levitation (ADL), which is one of the levitation techniques, enables levitating high-temperature melts under normal pressure of inert atmosphere. Surface tension and viscosity of high temperature melts can be obtained using the ADL techniques. In the ADL technique, the sample with a diameter of 1.5 to 2.5 mm levitates due to supplying inert gas through the conical nozzle. The levitated sample is heated and melted by irradiation of laser. The surface tension and viscosity of the levitated melts can be evaluated from the oscillation frequency and oscillation damping of the fundamental surface oscillation of the levitated melts. The fundamental oscillation of the levitated melts is excited acoustically using two opposite speakers installed at the gas inlet for the levitation of the melts [1-2]. Details of the measurement techniques and recent results of surface tension and viscosity measurements of FeS-Cu<sub>2</sub>S alloy melts will be presented at the conference.

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## Concentrated Solar Catalytic Dry Reforming of Methane and Carbon Dioxide over Ni Loaded Metal Oxides

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Dry reforming of methane (DRM) has been investigated for more than a century, the paramount stumbling block in its industrial application is the inevitable sintering of catalysts and excessive carbon emissions at high temperatures. However, the low-temperature DRM process still suffered the poor reactivity and severe catalyst deactivation from coking. We successfully regulated the relationship between two core competition reactions through light irradiation during photothermal dry reforming of methane over Ni/Ga<sub>2</sub>O<sub>3</sub>, resulting in the promotion of H<sub>2</sub> formation and the suppression of the reverse water gas shift reaction. The H<sub>2</sub>/CO ratio from 0.55 to 0.94 could be achieved. Furthermore, the combination of density functional calculations and X-ray photoelectron spectroscopy revealed that light irradiation impelled the direction of electron transfer to be reversed from Ga<sub>2</sub>O<sub>3</sub> to Ni to form the Ni<sup>0</sup> sites, which provided abundant hot electrons generating from the electronic interband transition of Ni to boost the formation and desorption of H<sub>2</sub>. In addition, we proposed a concept that highly durable DRM could be achieved at low temperatures via fabricating the active sites integration with light irradiation. The active sites with Ni-O coordination (Ni<sub>SA</sub>/CeO<sub>2</sub>) and Ni-Ni coordination (Ni<sub>NP</sub>/CeO<sub>2</sub>) on CeO<sub>2</sub>, respectively, were successfully constructed to obtain two targeted reaction paths that produced the key intermediate (CH<sub>3</sub>O\*) for anti-coking during DRM. In particular, the *operando* diffuse reflectance infrared Fourier transform spectroscopy coupling with steady-state isotopic transient kinetic analysis (*operando* DRIFTS-SSITKA) was utilized and successfully tracked the anti-coking paths during DRM process for the first time. It was found that the path from CH<sub>3</sub>\* to CH<sub>3</sub>O\* over Ni<sub>SA</sub>/CeO<sub>2</sub> was the key path for anti-coking. Furthermore, the targeted reaction path from CH<sub>3</sub>\* to CH<sub>3</sub>O\* was reinforced by light irradiation during the DRM process. Hence, the Ni<sub>SA</sub>/CeO<sub>2</sub> catalyst exhibits excellent stability with negligible carbon deposition for 230 h under thermo-photo catalytic DRM at a low temperature of 472 °C, while Ni<sub>NP</sub>/CeO<sub>2</sub> shows apparent coke deposition behavior after 0.5 h in solely thermal-driven DRM. The findings are vital as they provide critical insights into the simultaneous achievement of low-temperature and anti-coking DRM process through distinguishing and directionally regulating the key intermediate species.

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## Sorption Property of Sr<sup>2+</sup> on Seaweed-like Sodium Titanate Mat Synthesized by Hydrothermal Method

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Layered sodium titanates are a promising inorganic sorbent for removing toxic cation removal from wastewater. The Na<sup>+</sup> ions in interlayer of sodium titanate can exchange with cationic polluting species in wastewater. Sodium titanates are well known to exhibit various chemical formulas and crystal structures,

and its ion-exchange properties have been reported [1]. However, although the sorption mechanism of sodium titanate has been reported in several literatures, the relationship between the sorption behavior of cations and crystallographic properties has not been fully elucidated. Herein, we present a unique seaweed-like sodium titanate mat (SST) with randomly distributed layered sodium dititanate ( $H_xNa_{2-x}Ti_2O_5$ ) nanofibers synthesized by a simple hydrothermal process [2]. Furthermore, from the viewpoint of crystallographic properties,  $Sr^{2+}$  sorption mechanism of SST was compared with that of sodium trititanate ( $H_xNa_{2-x}Ti_3O_7$ ) synthesized by the same method with adjusted NaOH concentration [3]. SST and micro-sized trititanate fibers were synthesized by the hydrothermal method at 200 °C, and batch tests were conducted at 25 °C for 1 day using 0.2-4.0 mmol/dm<sup>3</sup>  $SrCl_2$  solution to investigate the sorption amount of  $Sr^{2+}$ . The  $Sr^{2+}$  sorption isotherm of SST and trititanate were fitted with the Langmuir isotherm model, and these maximum sorption amounts were calculated as 2.1 mmol/g and 0.5 mmol/g, respectively. That is, the sorption density of SST was higher than that of trititanate.  $Sr^{2+}$  removal in SST was mainly caused by the ion-exchange reaction, while  $Sr^{2+}$  removal in trititanates was due to the ion-exchange reaction and the precipitation of  $SrCO_3$  by increasing pH. After sorption tests, almost all of the  $Na^+$  in dititanate (SST) with lamellar structure was released by the ion-exchange reaction, while some  $Na^+$  remained in the trititanate. This was presumably due to the zigzag layered structure of trititanate, which has two sites with different ease of  $Na^+$  ion exchange. In contrast, lamellar structure with linear arrangement of SST showed high selectivity for the ion-exchange reaction for  $Sr^{2+}$  and suppressed the pH increase. As a result, it was concluded that SST is less likely to induce precipitation reaction compare with trititanate. These differences in reactivity are strongly influenced by the layered crystal structure of sodium titanates, indicating that the design of the crystal structure of sodium titanate is important for controlling the sorption mechanism and improving the sorption efficiency.

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## Enhancement of Electrocatalytic Behavior of Metallic Organic Frame Works for Water Splitting at Elevating Temperature Measurements

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Several strategies have been adopted to enhance the electrochemical features of metal organic frameworks structures for water splitting. Herein, molybdenum based Zeolitic Imidazolate frameworks (ZIF-67) electrocatalysts were synthesized by solvothermal treatment at 200 °C for 18 hours. Different molybdenum contents were employed and N, N-Dimethylformamide and hexane was used as a liquor solvent. Several structure analysis techniques were adopted for the confirmation of structure and electrochemical measurements for the HER and OER process were performed in 1 M KOH solution at room temperature, 40 °C, 60 °C and 80 °C. Greater metal contents of molybdenum significantly enhanced the current density. Mo/4-ZIF-67 (4g molybdenum contents) exhibited the overpotential of 232 mV to approach the current density of 10 mAcm<sup>-2</sup> at room temperature and the overpotential reduced effectively to 93 mV at the temperature of 80 °C for the hydrogen evolution reaction HER process. Mo/4-ZIF-67 showed the Tafel slope of 95 mVdec<sup>-1</sup> in 1 M KOH solution. Mo/4-ZIF-67 (4g molybdenum contents) exhibited the overpotential of 358 mV to approach the current density of 10 mAcm<sup>-2</sup> at room temperature and the overpotential reduced effectively to 221 mV at the temperature of 80 °C for the oxygen evolution reaction (OER) process. Mo/4-ZIF-67 showed the Tafel slope of 95 mVdec<sup>-1</sup> in 1 M KOH solution and followed the Volmer-Heyrovsky mechanism. Temperature elevation influenced and caused remarkably to enhance the HER and OER characteristics of the molybdenum based ZIF structures. The enhancement of the HER and OER characteristics for water splitting may be attributed due to reduction of charge transfer and solution resistance at the elevating temperature. Moreover, density functional theory reveals that, active hydrogen adsorption-desorption process occurs at the metal sites and Mo/4-ZIF-67 exhibited the minimal Gibbs Free energy, which caused for a good HER and OER activity. Furthermore, the electrocatalyst, Mo/4-ZIF-67 maintained the current density for long time at room temperature as well as higher temperature. The results reveal that the Mo/4-ZIF-67 is an efficient electrocatalyst for water splitting.

## High-performance See-through Power Windows

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Thin-film solar cells made with polymer and perovskite absorbers represent a transformative technology with great potentials for high-throughput manufacturing at very low cost. In this talk, we will discuss the integrative approach of combining molecular design, interface and device to access high-performance polymer and perovskite solar cells, including the results of champion organic solar minimodules made in lab that have been published in the "Solar Cell Efficiency Table" by Prof. Martin Green (59th, 60th, 61st and 62nd editions), as well as our efforts in fabricating inverted perovskite solar cells with the certified efficiency over 26%.

Specific emphasis will be placed on the development of See-through power windows via a new design of semitransparent organic solar cells (ST-OSCs), which allows for the efficient utilization of spectrum-engineered solar photons from the visible to infrared range with both energy generation and saving features. Model analysis indicated that the installation of these see-through power windows worldwide would contribute to the carbon neutrality of society.

**Keywords:** n-Doping, Interfacial layer, Solar cell, Semitransparent

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## Microplastic Degradation by Advanced Oxidation Processes

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In this study, we contributed to a pioneering exploration by integrating Fenton oxidation and hydrothermal (HT) hydrolysis for synergistic degradation of microplastics over nanostructured catalysts. [1-3] To this end, spring-like carbon nanotubes were fabricated bearing high-level nitrogen dopants and encapsulated metal nanoparticles. The robust and magnetic carbon hybrids exhibited an outstanding catalytic performance in activation of peroxymonosulfate (PMS) to generate reactive radicals for MPs degradation. The spiral architecture and highly graphitic degree guaranteed the superb stability of the carbocatalysts in HT environment. The toxicity tests indicated that the organic intermediates from MPs degradation were environmental-benign to the aquatic microorganisms and can serve as a carbon source for algae cultivation. The outcomes of this study dedicate to providing a novel and green strategy by integrating state-of-the-art advanced oxidation technologies for remediation of MP contamination in water. [4,5]

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## Nanoporous Metal-Organic Frameworks (MOFs) Catalysts for Biomass and Plastics Conversion

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Scientific innovation in various fields is surely necessary to achieve carbon neutrality by 2050. To reduce carbon dioxide (CO<sub>2</sub>), seven approaches including de-fossil resources, switch to renewable energy, etc. have been proposed. Meanwhile, nanoporous metal-organic frameworks (MOFs) have been well known and have shown great potential in catalysis and energy applications owing to their high surface areas, controllable composition, and tunable surface functionalities. In this talk, I will focus on MOFs-driven carbon neutral society by introducing MOFs in heterogeneous catalysis for producing (1) several valuable fine chemicals such as BTX, FDCA, DMF from waste lignocellulosic biomass and (2) hydrogen gas from waste plastics. (1) For biomass-to-fine chemicals production, we synthesize a heterogeneous Bi-BTC catalyst for the conversion of bio-based 2,5-dimethylfuran and acrylic acid to para-xylene with a promising yield (92%), under relatively mild conditions (160 °C, 10 bar) with low reaction energy barrier (47.3 kJ/mol). The proposed reaction strategy also demonstrated remarkable versatility for furan derivatives such as furan and 2-methylfuran. (2) For plastics-to-H<sub>2</sub> production, MOF-derived NiO@CeO<sub>2</sub> catalyst with the self-decoking property was synthesized and applied. The highest hydrogen yield of LDPE using 30NiO@CeO<sub>2</sub> was achieved (137.0 mmol/g<sub>PE</sub>), and no carbon was generated. We also investigated the impact of different types of post-consumer plastic waste (including LDPE, HDPE, PP, PS, PET), and the production of LDPE waste was 136.4 mmol/g<sub>PE</sub>. 30NiO@CeO<sub>2</sub> catalyst can be reused for at least five times, and the hydrogen production in the fifth run was 100.8 mmol/g<sub>PE</sub>.

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## N-Doped Graphitic Carbon Nitride and Potassium Dichromate: A Rapid Approach Towards Humic-Like Substance Formation

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The role of potassium dichromate (Cr(VI)) in catalyzing the conversion of polyphenols to organic polymers, which is essential for humification in soils, is well-established. However, the oxidative polymerization process involved in this conversion is not fully understood and is time-consuming in its natural state. To study the effect of nitrogen (N) doping substances on the oxidative polymerization of phenolic compounds, we investigated the interaction between graphitic carbon nitride (C<sub>3</sub>N<sub>4</sub>), hydroquinone (HQ), and potassium dichromate. The introduction of C<sub>3</sub>N<sub>4</sub> resulted in the production of N-doped compounds and significantly accelerated the reaction rate beyond initial expectations. This enhanced efficiency can be attributed to the unique electronic structure and high nitrogen content of C<sub>3</sub>N<sub>4</sub>, which acts as a Lewis base and provides a scaffold for the reaction. The large surface area and abundant nitrogen sources of C<sub>3</sub>N<sub>4</sub> facilitate efficient electron transfer, leading to faster reaction rates and accelerated browning reactions compared to conditions without C<sub>3</sub>N<sub>4</sub>. These findings suggest that incorporating N-doping chemicals into the oxidative polymerization of HQ, in combination with Cr(VI), offers a promising approach for the rapid formation of humic-like substances. The use of N-containing catalysts in this method provides a valuable means to investigate HQ oxidation reactions and advance our understanding of humic substance formation.

## Temperature-dependent structural behavior of cobalt/nickel selenite hydrates as solar water evaporators

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As the world's population continues to grow and climate change progresses, the need for clean water is becoming increasingly urgent. Water desalination plays a vital role in addressing the challenges posed by freshwater scarcity in arid regions. The development of cost-effective and sustainable methods to obtain freshwater has become paramount, and solar water evaporation has emerged as a promising approach among traditional water purification technologies [1]. Recently, an investigation of the new class of solar water evaporators based on selenite hydrates (based on earth-abundant Ni and Co) has shown that the combination of the high absorptance in the full solar spectrum (96 %) and hydrophilicity, makes



selenite hydrates a promising material for solar steam generation. Both compounds demonstrated a higher evaporation rate than most reported 2D evaporators –  $1.83 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for  $\text{NiSeO}_3(\text{H}_2\text{O})_2$  and  $2.34 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for  $\text{CoSeO}_3(\text{H}_2\text{O})_2$ . The superior water transport has been taken to originate from the water of hydration within these selenite hydrates, since the presence of water within the structure can form ligand bonds with other water molecules coming from the water source. To clarify the mechanism of water transportation and to understand the reason for the evaporation rate difference between  $\text{NiSeO}_3(\text{H}_2\text{O})_2$  and  $\text{CoSeO}_3(\text{H}_2\text{O})_2$ , in this study thermogravimetric analyses were performed to examine the thermal stability and phase variation with further structural characterizations. Based on the observed compositional mass loss due to nonstoichiometric alterations,  $\text{NiSeO}_3(\text{H}_2\text{O})_2$  and  $\text{CoSeO}_3(\text{H}_2\text{O})_2$  nanomaterials were heated up to 40, 70, 100, 200, and 400 °C, respectively and the structures and compositions were characterized by X-ray diffraction (XRD) and Raman spectroscopy. For  $\text{NiSeO}_3(\text{H}_2\text{O})_2$ , along with the heating a surface lattice reconstruction could be found due to the dehydration of surface water at lower temperatures less than 100 °C, and at higher temperatures, the process of removing internal hydrated water started to be dominant with less influence from the environment, which thus caused an internal transportation of hydrated water within the material. The  $\text{CoSeO}_3(\text{H}_2\text{O})_2$  material remained more stable at higher temperatures than  $\text{NiSeO}_3(\text{H}_2\text{O})_2$  and even at 200 °C kept the structure. Owing to the different ligand fields  $\text{CoSeO}_3(\text{H}_2\text{O})_2$  shows higher lattice distortions and minor surface reconstructions compared to  $\text{NiSeO}_3(\text{H}_2\text{O})_2$ . During applications of the solar water evaporators, the temperature of the systems may increase, and the decrease in energy requirements for water transportation may lead to a higher evaporation rate, as well as an abundant and consistent water supply from the water source, and, as a result, to the effective solar water evaporation.

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## Trace Gases and Particulate Matter Emitted During Thermal Treatment of Waste Silicon Solar Panels for Extraction of Materials

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End-of-life (EOL) Photovoltaic (PV) modules must be properly recycled to recover resources, advance a circular economy, and subsequently lessen the environmental impact. So far, different mechanical, chemical and thermal treatment methods for recycling have been suggested and reported. However, thermal treatment is the most followed approach for recycling EOL PV modules. In the present investigation, waste silicon solar panels were thermally treated at a high temperature of 600°C to extract various elements from it and also to study the various types of emissions during the process. The thermal treatment involves the decomposition of polymeric layers leads to the emission of trace gases  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{CH}_4$  and particulate matter (PM), which may harm human health and environment. The effects of thermal treatment on the environment were studied by calculating the emission factor (EF) of released trace gases, particulate matter (PM), organic carbon (OC), elemental carbon (EC), and water-soluble organic carbon (WSOC). A total of 13 elements were detected by XRF spectroscopy which was emitted during the thermal treatment of waste silicon solar panels: Na, B, Ca, N, Mg, Al, P, K, S, Fe, Cl, Cr, and Ag. After considering various kind of emission during thermal treatment, it will be great to recover polymeric layers from EOL PV modules rather than its decomposition. It will not only solve the emission issue but also add some economic value in the form of material recovery.

**Keywords-** Solar waste, Recycling, Thermal Treatment, Emission, Gases, Recovery.

# Poster Presentations

## Achieving Cardiac Transdifferentiation through miRNA Delivery via Scaffold

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Electrospun polymeric scaffolds are ideal for delivering drugs and biomolecules in advanced regenerative applications as they can mimic the extracellular matrix. Cardiac tissue engineering is a promising area for these scaffolds, but delivery system limitations and reprogramming efficiency must be addressed. This study focuses on developing a functional scaffold that can directly reprogram adult human cardiac fibroblasts into cardiomyocyte-like cells. Two distinct topologies of electrospun PLLA are used to achieve sustained delivery of two muscle-specific microRNAs. Polyethyleneimine forms stable PEI-miRNA complexes through electrostatic interactions, which are then immobilized on the electrospun smooth and porous scaffolds. The loading efficiency is high, with approximately 96% and 38% observed for fibronectin-modified and unmodified surfaces, respectively. The in-vitro release experiment shows a biphasic pattern of PEI-miRNA polyplexes from the scaffolds. Overall, these dual miRNA scaffold systems precisely control the cardiac fibroblast cell fate by combining topographic cues of electrospun fibers and dual miRNAs, making them an excellent formulation for achieving optimal results.

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## Green Chemistry Advancement: Unravelling Dye Removal Potential Using Nitrogen-Doped Palm Oil Mill Effluent Sludge-Biochar as Peroxydisulfate Activator

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Transition metal-based homogeneous or heterogeneous catalysts have been studied for activating persulfate and shown to be a good alternative for the activation of persulfate in organic pollutant recalcitrants. Nevertheless, a significant problem with these catalysts is the secondary contamination due to metal leaching during the process. Therefore, researchers have drawn their attention to nitrogen-doped biochar as a promising alternative persulfate activator due to its lower cost and being more environmentally friendly.

In this study, the researchers focused on synthesising nitrogen-doped biochar from Palm Oil Mill Effluent sludge (POS). In Malaysia, POS generated an average of 2.2 million tonnes annually and was disposed of and utilised as fertiliser, which indirectly created secondary pollution to the soil. Various studies have reported the feasibility of Palm Oil Mill Effluent sludge biochar (POSB) in the removal of inorganics; however, no research has investigated the efficacy of POSB as a peroxydisulfate (PDS). The POS were prepared through a simple pyrolysis process and doped with Urea at different temperatures ranging from 400°C to 700 °C under nitrogen conditions and used to activate peroxydisulfate (PDS). This study was conducted based on three ratios of the urea-doped process, which were 25:75, 50:50, and 75:25 N-doped POSB. The surface characterization of the POSB exhibited successful doping of urea into the biochar materials. POSB at 700 oC has greater catalytic activity than POSB at 400°C. Dye was completely degraded within 60 minutes of reaction time using 1 g of 75:25 Urea-doped POSB at 700°C, 3 mM PDS, and a pH 5 initial solution as the optimum operating parameters. The pseudo-first-order kinetic model accurately described the dye degradation kinetics. This research demonstrates the efficacy of non-metallic nitrogen-doped biochar as a green-catalyst in the removal of dye in wastewater treatment technology and simultaneously reduces the disposal of POS onto soil that leads to soil pollution.

## Infrared FT-IR Insight Into Prolonged Exposure to Ambient Air of Semiconductor Kesterite $\text{Cu}_2\text{ZnSnS}_4$ Nanopowders Prepared via Mechanochemical Synthesis Route

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A quaternary sulfide  $\text{Cu}_2\text{ZnSnS}_4$  (kesterite), thanks to accessibility and friendly environmental features, is a prospective semiconductor for applications in photovoltaic cells. The actively absorbing sunlight thin kesterite films made via kesterite nanopowder-containing inks or by sputtering techniques face various challenges associated with the often overlooked “oxygen aspect” – the role of sulfur-substituted oxygen centers and the compound’s susceptibility to oxidation when exposed to ambient air. In our approach to study this aspect, we prepared a pool of kesterite nanopowders using three different precursor systems via a convenient mechanochemical synthesis method [1]. These systems were composed of (i) metals and sulfur { $2\text{Cu}+\text{Zn}+\text{Sn}+4\text{S}$ }, (ii) metal sulfides and sulfur { $\text{Cu}_2\text{S}+\text{ZnS}+\text{SnS}+\text{S}$ }, and (iii) initially made in-situ copper alloys by high energy ball milling of the metals { $2\text{Cu}+\text{Zn}+\text{Sn} \rightarrow$  copper alloys}, which further were reacted with sulfur { $+4\text{S}$ }. The freshly made nanopowder, tentatively called prekesterite, is crystallographically cubic and defunct of semiconducting properties. The thermal annealing of prekesterite at 500 °C results in the tetragonal semiconductor kesterite.

All nanopowders were studied as freshly made and then after one, three, and six months of exposure to ambient air. Based on XRD examination, already after one-month exposure some 30-40 wt% of either prekesterite or kesterite nanopowders showed clear signs of oxidation with the formation of hydrated metal sulfates  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ , and tin(IV) oxide  $\text{SnO}_2$ , and this process continued through the sixth month to oxidize as much as 50 to 70 wt% of both forms, independent on the precursor system. The infrared FT-IR spectra confirmed in the fresh materials either no detectable quantities or merely traces of the metal sulfates with the latter forming due to an inevitable sample exposure to air during preparation and measurements. However, the hydrated copper and zinc sulfate oxidation products were clearly identified after one-month air exposure to be further enhanced for the materials after three and six-month exposure. The presence of  $\text{SnO}_2$  could not be ascertained by this method because of the superposition of the strong metal sulfate-originated bands and the expected O-Sn-O vibrations in the  $600 \text{ cm}^{-1}$  range. On the other hand, the formation of the hydrated forms of the sulfates was clearly manifested by the growing with exposure time broad band in the  $3300\text{-}3500 \text{ cm}^{-1}$  range characteristic of water molecules. Interestingly, the FT-IR spectra for the starting metal sulfides,  $\text{Cu}_2\text{S}$ ,  $\text{ZnS}$ , and  $\text{SnS}$ , similarly run for the fresh powders and for the powders after air exposure for 2 weeks and for one month, showed for  $\text{Cu}_2\text{S}$  visible oxidation to the copper sulfate already after two weeks whereas even one month exposure of  $\text{ZnS}$  and  $\text{SnS}$  did not yield any signs of oxidation. The enhanced oxidation susceptibility of the copper centers may thus initiate the destructive water vapor-assisted oxidation of the kesterite nanopowders.

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## Micro-Raman Spectroscopy used to Follow Oxidation in Ambient Air of Semiconductor Kesterite $\text{Cu}_2\text{ZnSnS}_4$ Nanopowders Made by Mechanochemically-assisted Synthesis Route

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The complex metal sulfide  $\text{Cu}_2\text{ZnSnS}_4$ , called kesterite, has been widely considered as silicon contender in photovoltaic cell applications. In this regard, kesterite nanopowders can be used for making special inks or as a sputtering source for the preparation of thin sunlight adsorbing layers. Their susceptibility to oxidation is a challenging issue given a projected prolonged exposure to ambient air. In the study aimed at addressing the oxygen aspect in kesterite preparation/examination/storage, we prepared various kesterite-type nanopowders with a mechanochemically-assisted synthesis method using "wet" milling conditions (xylene) and three different precursor systems [1]. The as-prepared nanopowders are of cubic polytype, tentatively called by us prekesterite, and do not show semiconductor properties whereas their annealing at 500 °C results in tetragonal semiconductor kesterite. All prekesterites and kesterites were subjected to a time-controlled exposure to ambient air. The selected properties were examined for the fresh, one month, and six month-exposed materials.

For the freshly made nanopowders, the micro-Raman spectra of the prekesterites from three different precursor systems are very similar. In the diagnostic range of 250-400  $\text{cm}^{-1}$  containing a band cluster, there is one strong peak at 331-333  $\text{cm}^{-1}$  (A symmetry) and two lower intensity, broad, and superimposed peaks at 294-296  $\text{cm}^{-1}$  and 360-365  $\text{cm}^{-1}$  (A symmetry and B symmetry, respectively). There is also a low intensity, broad peak at ca. 660  $\text{cm}^{-1}$  that is assigned as the second order Raman mode. For the kesterite samples, the overall appearance of the spectra matches that of the respective prekesterites but with the bit sharper and better shaped-up peaks, now, at 333-335  $\text{cm}^{-1}$ , 298-300  $\text{cm}^{-1}$ , and 360-365  $\text{cm}^{-1}$ . Also, detected in all kesterite samples is the weak and broad second order Raman mode at ca. 660  $\text{cm}^{-1}$ . The similarity of the Raman spectra for the prekesterites and kesterites is consistent with their similar chemical and lattice phonon-type characteristics. A specific feature of the kesterite spectra is the presence of a weak to medium intensity and partially overlapped bands at ca. 1350 and 1570  $\text{cm}^{-1}$ , which likely correspond to the D and G bands, respectively, in amorphous carbons formed from pyrolysis of remnant xylene.

For all nanopowders exposed to ambient air for up to six months, the kesterite-specific-part of the spectra in the range ca. 250-400  $\text{cm}^{-1}$  does not qualitatively change with time whereas some new features appear, which are especially pronounced for the longest time. A new cluster of the overlapped weak peaks at ca. 430-500  $\text{cm}^{-1}$  and a broad weak peak at ca. 1040  $\text{cm}^{-1}$  can convincingly be assigned to the presence of  $-\text{SO}_4$ -Raman bands in the hydrated metal sulfates, respectively, as  $\nu_2$  bending vibrations and  $\nu_1$  symmetric stretches. Concluding, Raman spectroscopy confirms the progress of the specific kesterite oxidation in ambient air towards metal sulfates.

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## Impact of Temperature on Optical Properties of Oxyfluorotellurite Glasses Doped with Praseodymium

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The thermal stability of oxyfluorotellurite glass systems  $(65-x)\text{TeO}_2\text{-}20\text{ZnF}_2\text{-}12\text{Pb}_2\text{O}_5\text{-}3\text{Nb}_2\text{O}_5\text{-}x\text{Pr}_2\text{O}_3$  doped with praseodymium was examined. The different concentrations of praseodymium oxide ( $x = 0.5$  and 2 mol%) were applied to verify the thermal, optical and luminescence properties of the materials under study.

Differential thermal analysis (DTA) yielded favorable results in terms of glass thermal stability which is improved with increasing dopant concentration i.e. (higher values of thermal stability parameters  $\Delta T$ ,  $H'$  and  $S$ ).

The temperature dependences of optical absorption and emission spectra in the temperature range 300 - 675 K for VIS-NIR region were investigated. The involved  $\text{Pr}^{3+}$  optical transition intensities and relaxation dynamic of praseodymium luminescent level were determined.

The ultrashort femtosecond pulses were utilized to examine a dynamic relaxation of the praseodymium luminescent levels. Although, the measured emission of the optically active ions in the studied glass encompasses the quite broad spectral region, the observed luminescence may be attributed to  $^3\text{P}_1$  excited states. As result, the observed decrease of the experimental  $^3\text{P}_0$  level lifetime with growing activator concentration was identified as an enhancement of Pr-Pr interaction that is responsible for a self-quenching of  $\text{Pr}^{3+}$  luminescence in a glass host.

Application potential of the investigated material in optical sensor thermometry was evaluated. The maximum absolute and relative sensitivities were established at  $5.1 \times 10^{-3} \text{ K}^{-1}$  at  $T = 460 \text{ K}$  and  $0.46 \% \text{ K}^{-1}$  at  $T = 300 \text{ K}$  ( $I_{530}/I_{497}$ ) and  $8.7 \times 10^{-3} \text{ K}^{-1}$  at  $T = 675 \text{ K}$  and  $0.20 \% \text{ K}^{-1}$  at  $T = 600 \text{ K}$  ( $I_{630}/I_{497}$ ), respectively.

## Susceptibility to Metal Working Processes of High-strength CuMg Alloys Assessed with Finite Element Method

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Modern industry is focused among others but not limited to the efficiency of the manufacturing process. Which is why, when a new material is being designed it is necessary to assess its susceptibility to prospective metal working processes to the form of a final product. Conductive materials with copper matrix usually find their origin in various casting lines and the obtained cast rods or ingots are used as batch material for further drawing or cold/hot die forging processes. The study presents results concerning numerical analysis of the metal working processes of CuMg alloys with various Mg content (2 - 4 wt. %). Using Finite Element Method (FEM) simulations possibility of fracture occurrence was determined during plastic working. The analysis of the obtained results made it possible to verify the best geometry of the tools, i.e. the drawing half angle and the bearing length of the drawing die, as well as the optimal shape of the forging die limiting the flash. The abovementioned is necessary in order to create a satisfactory replacement for other copper alloys in energy industry, such as expensive CuAg or CuNiSi alloys or providing low electrical conductivity such as bronzes or brasses. All the analyses were based on the experimental data regarding the Yield Strength and Ultimate Tensile Strength of the alloys in order to estimate whether or not the fractures would occur and thus the possibility of subjecting the designed materials to prospective metal working processes.

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## Penta Nitrogen Coordinated Cobalt Single Atom Catalysts with Oxygenated Carbon Black for Electrochemical H<sub>2</sub>O<sub>2</sub> Production

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The two-electrons (2e<sup>-</sup>) oxygen reduction reaction (ORR) offers a sustainable and decentralized alternative to the traditional synthetics for hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) production. Although various Co single atom catalysts (SACs) have been proposed as highly effective 2e<sup>-</sup> ORR catalysts, there is still room for improvement through fine-tuned coordination environment. Here, a Co-N<sub>5</sub>-O-C with the combination of highly coordinated Co-N<sub>5</sub> moieties and nearby electro-withdrawing epoxides is first time developed to reach the optimal binding energy of \*OOH intermediate, resulting in the ultrahigh mass activity of 87.5 A g<sup>-1</sup> at 0.75 V vs. RHE. Moreover, a high H<sub>2</sub>O<sub>2</sub> production rate of 11.3 mol g<sup>-1</sup> h<sup>-1</sup> at 200 mA cm<sup>-1</sup> is also obtained by a flow cell device. Such an efficient in-situ generation of H<sub>2</sub>O<sub>2</sub> further enables 100% degradation of the organic methylene blue pollutant within 15 min through the electro-Fenton process. These findings will provide a new direction for on-site H<sub>2</sub>O<sub>2</sub> synthesis and wastewater treatment.

## Comparative Studies for the Effect of Different Pore Surface Area and Center Metal Species of Mono-metallic and Bi-metallic MOF Materials in the Application of Gas Sensing Devices

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This research is to investigate the sensing effect of mono-metallic and bi-metallic metal organic framework (MOF) materials with different central metals and surface areas applied to hydrogen sulfide gas sensing. First, three different mono-metallic MOF (*i.e.*, MIL-88B-Fe, MIL-100-Fe, and HKUST-1-Cu), were prepared first, and were easily synthesized at room temperature. Subsequently, one bi-metallic MOF-919 (Fe-Cu) was also prepared under 100 °C. The as-prepared four distinctive MOF materials was characterized by FTIR, XRD, SEM, BET, and XPS. Moreover, the redox and doping/de-doping capability of four MOF materials was investigated by electrochemical CV and UV-visible absorption spectrophotometer, respectively.

In the application of MOF in sensing device of hydrogen sulfide gas, MIL-100-Fe (surface area (*a*) = 1342.26 m<sup>2</sup>/g) was found to show better sensing response to H<sub>2</sub>S gas (*r* = 564.83 %) than that of MIL-88B-Fe (*a* = 200.61 m<sup>2</sup>/g, *r* = 223.12 %), indicating that the Fe-containing of MOF with larger surface area exhibited better performance. On the other hand, the surface area (*a* = 719.42 m<sup>2</sup>/g) of HKUST-1-Cu was found to show the sensing response of 650.40 %, reflecting that central atom of Cu in HKUST-1-Cu revealed higher/dominant sensing response than that of central atom of Fe in MIL-100-Fe, even the Cu-containing MOF with lower surface area. Moreover, the sensing response to H<sub>2</sub>S gas (*r* = 931.15 %, *a* = 1461.07 m<sup>2</sup>/g) of bi-metallic MOF was better than that of the other three due to the synergistic effect of bi-metals.

## Comparative studies of Inorganic Iron-containing MOF, Organic ACAT, and Corresponding Organic-inorganic Composite in H<sub>2</sub>S Gas Sensing Application

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In this study, the comparative study of inorganic iron-containing organometallic framework (MOF), MIL-88B(Fe), organic amine-capped aniline trimer (*i.e.*, ACAT) and organic-inorganic composite in H<sub>2</sub>S gas sensing application was investigated. Firstly, organic ACAT was synthesized by the “oxidative coupling method”, followed by characterized by <sup>1</sup>H-NMR, FTIR, and MS. On the other hand, MIL-88B(Fe) was prepared by solvothermal method. Moreover, the composite of ACAT-MIL-88B(Fe) was prepared by blending MIL-88B(Fe) with 1 wt-% of as-prepared ACAT. Structure of MIL-88B(Fe) and corresponding composite was identified by powder XRD, SEM and BET. Hydrogen bonding was can be found between the carbonyl group of MIL-88B(Fe) and amine group of ACAT, as evidenced by FTIR spectrum. Surface area ( $a = 205.8 \text{ m}^2/\text{g}$ ) of MIL-88B(Fe) was found to be much larger than that of ACAT-MIL-88B(Fe) ( $a = 51.8 \text{ m}^2/\text{g}$ ) based on the BET data, indicating that the introducing of 1 wt-% of ACAT into MIL-88B(Fe) may decrease the surface area of MOF.

In the studies of gas sensing applications, the detection concentration range of hydrogen sulfide gas is fixed between 1 ppm and 10 ppm. It can be found that sensing response to H<sub>2</sub>S gas of organic-inorganic composite was found to be significantly higher than that of inorganic MIL-88B(Fe) and organic ACAT, respectively. It indicated that although the incorporation of ACAT into MIL-88B(Fe) may decrease the surface area of MOF, it still can promote the sensing response to H<sub>2</sub>S gas of MIL-88B(Fe).

## Ordered Mesoporous Intermetallic with Enhanced Electrocatalytic Activity and Stability for Hydrogen Evolution

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Ordered mesoporous noble metals (NMs) have displayed unique catalytic and electrocatalytic performance distinctive from traditional nanoparticles. Despite great efforts, the range of mesoporous NMs is mainly limited to single metals and their metal alloys with random atomic arrangements. Herein, we have reported, for the first time, a novel series of high-performance MI-PtZnM and MI-PtX<sub>2</sub> electrocatalysts with high orderliness in macroscopic, mesoscopic, and atomic levels. The synthesis relies on a precise Pt-to-PtZnM/PtX<sub>2</sub> phase evolution confined within a rigid/thermally stable and ordered mesoporous KIT-6 through a concurrent template strategy. The samples feature rhombic dodecahedral morphology, ordered gyroid mesostructure, and cubic/hexagonal intermetallic phase. These features thus kinetically accelerate the dissociation of H<sub>2</sub>O and remarkably enhance electrocatalytic HER activity and stability.

Among the obtained results, Our MI-PtZnCo trimetals were also highly active and stable for HER electrocatalysis over a wide pH range (neutral and acidic media)<sup>[1]</sup>. Mechanism studies suggested that Co enabled Pt atoms of MI-PtZn with more electron-rich surface, in addition to stable mesoporous and intermetallic structure, synergistically accelerating Tafel kinetics and thus enhancing HER activity and stability of MI-PtZnCo trimetal electrocatalyst. In addition, we also report the first synthesis of four mesoporous intermetallic noble metal-nonmetal PtX<sub>2</sub> (X = P, S, Se, and Te) and three noble metal-metal-nonmetal MI-PtMP<sub>2</sub> (M = Ni, Co, and Fe) with the high macroscopic/mesoscopic and atomic orderliness<sup>[2]</sup>. The optimum MI-PtP<sub>2</sub> discloses ultrahigh mass/specific activity (3.31 A mg<sub>pt</sub><sup>-1</sup>/7.75 mA cm<sub>pt</sub><sup>-2</sup>) and superior stability (only 15.2% of mass activity loss after the accelerated durability test for 30000 cycles), suppressing the reported electrocatalysts. Our work opens up new opportunities for designing and synthesizing novel hierarchically ordered mesoporous electrocatalysts with targeted functions for a variety of applications.

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## Mesoporous palladium-nonmetal Alloy Nanocubes for Efficient Electrochemical Nitrate Reduction to Ammonia

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Developing highly active and selective electrocatalysts for electrochemical nitrate reduction reaction (NITRR) is very important for synthesizing recyclable ammonia (NH<sub>3</sub>) in an economic and environmentally friendly manner. Despite some encouraging progress, their activity and selectivity have been remarkably slower than expected. Here mesoporous palladium-nonmetal (meso-PdX) nanocubes (NCs) are reported as a new series of highly efficient electrocatalysts for selective nitrate reduction reaction (NITRR) electrocatalysis to NH<sub>3</sub>. The samples feature uniformly alloyed compositions and highly penetrated mesopores with abundant highly active sites and optimized electronic structures. The best meso-PdN NCs hold an outstanding NITRR activity and selectivity with a remarkable NH<sub>3</sub> Faradaic efficiency of 96.1%, suppressing the state-of-the-art electrocatalysts. Meanwhile, meso-PdN NCs are electrocatalytically stable, retaining well the activity and selectivity of NO<sub>3</sub><sup>-</sup>-to-NH<sub>3</sub> electrocatalysis for more than 20 cycles. Detailed mechanism studies ascribe the superior performance to combined compositional and structural synergies of meso-PdN NCs that not only promote the adsorption (reactivity) of NO<sub>3</sub><sup>-</sup> and the desorption of NH<sub>3</sub> but also increase the retention time of key intermediates for the deeper NITRR electrocatalysis to NH<sub>3</sub> through an eight-electron pathway.

## Catalytic Performance Enhancement of Post-modified Metal-Organic Frameworks for CO<sub>2</sub> Cycloaddition Reaction

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The rise in atmospheric CO<sub>2</sub> resulting from industrial growth is a key driver of global warming and a pressing environmental issue. Nevertheless, converting CO<sub>2</sub> into valuable products is sustainable due to its cost-effectiveness and abundance. One approach is combining CO<sub>2</sub> with epoxides to create useful cyclic carbonates. However, efficient catalysts are needed to activate CO<sub>2</sub> and epoxides effectively, and developing a recyclable catalyst with high activity under mild conditions, without co-catalysts or solvents, is crucial.

Metal-organic frameworks (MOFs) are promising for CO<sub>2</sub> coupling reactions due to their high surface area and catalytic potential. Among MOFs, MIL-101-SO<sub>3</sub>H (Cr), containing chromium and terephthalate sulfonic acid, is commonly used as an acid catalyst due to its abundant Brønsted acid sites (-SO<sub>3</sub>H) and Lewis acid sites from unsaturated Cr (III) ions. However, enhancing its catalytic performance is challenging because it lacks CO<sub>2</sub>-attracting Lewis base sites, often requiring harsh conditions or co-catalysts. Among MOFs, MIL-101-SO<sub>3</sub>H (Cr) is commonly used as an acid catalyst. It's rich in Brønsted acid sites (-SO<sub>3</sub>H) and benefits from Lewis acid sites provided by unsaturated Cr (III) ions. However, boosting its catalytic performance is challenging due to the absence of CO<sub>2</sub>-attracting Lewis base sites, often necessitating harsh conditions or co-catalysts.

Herein, we developed a novel method to improve the utilization of CO<sub>2</sub> by introducing Lewis base sites into the acid catalyst MIL-101-SO<sub>3</sub>H. We synthesized amine-functionalized MIL-101-SO<sub>3</sub>H catalysts using two different amine-containing ligands through an acid-base condensation reaction. Their catalytic performances for the CO<sub>2</sub> cycloaddition reaction have been evaluated under ambient conditions without the need for co-catalysts or solvents. The amine-functionalized catalysts exhibited significantly higher catalytic activities (100% conversion of epichlorohydrin with over 99% selectivity) than pristine MIL-101-



SO<sub>3</sub>H and previously reported catalysts for CO<sub>2</sub> cycloaddition. This improved performance is attributed to the synergistic effect of Lewis acid Cr sites and polar Brønsted acid sites, and the introduction of amine functional groups, which provide abundant CO<sub>2</sub>-attracting Lewis base sites through the proposed reaction mechanism accounts for the contributions of amine functional groups and Lewis acidity.

## Categorization of Data-driven Models to Improve Prediction Performance for Polypropylene Composite Development

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Recently, much research with machine learning (ML) method has emerged in material science. However, it is challenging to apply ML method to the blending process because there are numerous combinations of ingredients, such as a development process. In this research, categorization was proposed as a data preprocessing technique to consider the various types of ingredients in the model training process. Categorization involves grouping data with similar ingredients and handling data imbalances by creating categorized datasets. For implementation, polypropylene (PP) composite dataset, consisting of 803 data associated with two physical properties (flexural strength (FS) and heat deflection temperature (HDT)), has been applied. The dataset encompasses 90 types of ingredients and various blending ratios in each data, resulting in data imbalances that undermine property prediction accuracy. Through the categorization process, 494 and 495 distinct categories were generated for each physical property. Finally, to validate the impact of categorization on prediction performance, property prediction models were constructed using multi-linear regression (MLR), a conventional linear regression technique. FS and HDT were predicted using data before and after categorization, and the coefficient of determination (R<sup>2</sup>) was calculated and compared for the actual and predicted values. The comparison revealed an increase in R<sup>2</sup> values of 0.1044 and 0.0989 for FS and HDT, respectively, when predicting properties with post-categorization data. This result demonstrates that categorization improves the prediction performance by considering various types of ingredients in data-driven modeling. Thus, the proposed method help us to develop robust data-driven models in the PP composite development process.

**Keywords:** polypropylene composite, categorization, machine learning

## Construction of 2D Lamellar Membrane for Comprehensive Utilization of Solar Energy

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Energy plays a vital role in the process of human development. The continuous use of nonrenewable sources of energy, such as fossil fuels, has been detrimental to the climate and environment, forcing a re-examination of the viability of such forms of energy as a primary resource. Solar energy, recognized as the most abundant and sustainable source of renewable energy, has garnered increasing attention. In this study, a series of 2D lamellar membranes (2DLMs) was fabricated through vacuum-assisted self-assembly, with a specific emphasis on their combined application for photocatalytic hydrogen evolution (PHE) and photothermal water evaporation (PWE). Conventional BiOCl served as the typical 2D photocatalyst, while cellulose nanofibers (CNFs) or carbon nanotubes (CNTs) functioned as 1D materials to manipulate the water state and enhance light-to-thermal conversion efficiency. CNTs, serving as a carbon acceptor material, fulfilled dual roles as photoabsorbers and photocarrier transport channels, thereby significantly enhancing photocatalytic performance by converting light into heat energy. Concurrently, CNFs played a pivotal role in regulating the hydrogen bond network within water molecules, leading to a reduction in the enthalpy of

evaporation. As expected, the 2DLM constructed using BiOCl and CNF@CNT (BOC-CNF@CNT) rapidly attained a surface temperature of approximately 46.6 °C, coupled with a remarkable water evaporation rate of up to 2.05 kg·m<sup>-2</sup>·h<sup>-1</sup>. The average PHE rate achieved reached 25.42 μmol·g<sup>-1</sup>·h<sup>-1</sup>, which was 1.99-fold that of BiOCl-CNF 2DLM (BOC-CNF) and 1.42-fold that of BiOCl-CNT 2DLM (BOC-CNT). The objectives of this study extended beyond the mere resolution of the challenge of associated with recovering nanosized photocatalysts; it encompassed an overarching aim to enhance the efficiency of the photocatalysis process under conditions of partial ultraviolet sunlight absorption and utilization. Additionally, we conducted a comprehensive investigation into the effect of confined water on both PHE and PWE. The 2DLM, constructed in this work through a straightforward preparation method, holds the potential for large-scale production and exhibits promising application prospects.

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## Impact on Charge Distribution in Molecules by Nano-glass Surface

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Today, we would like to present examples of the impact of nano-glass surfaces on charge distribution in molecules. Nano-glass is an insulator, yet it has the potential to alter the charge distribution within molecules.

When aiming to enhance chemical reaction rates, common approaches involve increasing concentration/temperature and introducing catalysts. The rate constant of an electrophilic metal coordination reaction is accelerated by a factor of 23 on the surface of layered aluminosilicate (LAS). Here, the reaction substrate (ligand molecule) induces dielectric polarization due to the polar and anionic surface. According to the Arrhenius plot, the frequency factor (A) is increased by almost three orders of magnitude on the surface. This suggests that the collision efficiency between the ligands and metal ions is enhanced on the surface due to dielectric polarization. This is surprising because one side of the ligand is obscured by the surface, which would normally be expected to reduce collision efficiency.

This unique method of accelerating chemical reactions has the potential to expand the utility of LASs, which are chemically inert, abundant, and environmentally friendly. Furthermore, this concept is applicable to other metal oxides with polar surfaces, making it valuable for various future chemical reactions. Additionally, nano-glass can reduce the working voltage of an electrochromic device by neutralizing the cationic charge on the central metal. Layered silicate also improves the electrochemical responses of a metal complex polymer. This modulation of electrochemical properties by layered silicates could be applied to other electrochemical systems, including hybrids of redox-active ionic species and ion-exchangeable adsorbents.

## Self-Healing Polyurethane Nanocomposite Containing Aminated-Cellulose Nanocrystals

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The scientific community is showing a growing interest in nanotechnology and as a result, there are ongoing efforts to investigate and create practical uses for cellulose nanocrystals (CNCs) in industry. Cellulose, a natural polymer, has properties such as regeneration and biodegradability. In particular, CNCs have high crystallinity and low density, making them ideal raw materials for high-hardness, lightweight composites. The objective of this study is to investigate the surface characteristics of high-hardness and self-healing materials. However, there is a trade-off between mechanical strength and self-healing capability, making it challenging to produce high-hardness, self-healing materials. In this research, we report the surface modification of CNCs and a CNC-based self-healing polymer composite.

CNC was modified on its surface using aminopropyltriethoxysilane (APTES) to improve its dispersion in organic solvents. Then, CNC/polyurethane composites were prepared to increase hardness through condensation polymerization and interconnection of an isocyanate-terminated prepolymer, amine-functionalized CNC, and chain extender. The self-healing composite coating on the substrate 1) demonstrates high pencil hardness of HB. 2) The healing rate was observed to be over 70% when the volume of cracks was monitored before and after self-healing of the polymer coating using a confocal microscope. 3) The salt spray test confirmed that iron plates coated with the self-healable composite exhibit good resistance to corrosion, even after scratches and self-healing.

## Synthesis of Hollow Metal Hydroxide Nanoparticles Containing Cobalt and Iron from Metal Fluoride Nanoparticles

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In order to realize a hydrogen-based society, highly efficient electrocatalysts are indispensable, serving as alternatives to conventional precious metal catalysts in facilitating oxygen evolution reaction (OER). While cost-effective transition metal hydroxides have gained attention as alternative OER catalysts, their performance has not been sufficient for practical applications. One of the ways to enhance the catalytic activity is to control the nanostructure of the catalyst. In particular, catalysts structured with hollow nano morphologies hold significant potential for achieving heightened catalytic activity owing to the synergistic benefits derived from their hollow architecture, which affords excellent mass transport properties, and the expansive surface area provided by the nanoparticles.<sup>1</sup> However, synthesizing hollow nanoparticles of hydroxides is not easily achievable.

In this study, we successfully synthesized hollow nanoparticles containing cobalt and iron. The selection of metal hydroxides containing cobalt and iron was deliberate, as their compositional attributes hold promise for enhancing OER.<sup>2</sup> To synthesize hollow nanoparticles composed of metal hydroxides, we employed perovskite-structured metal fluoride  $KMF_3$  as a template. Because  $KMF_3$  is soluble in water, our approach initially transforms only the particle's surface into metal hydroxides, followed by the dissolution of any remaining unreacted  $KMF_3$ , ultimately resulting in the synthesis of hollow nanoparticles.

$KMF_3$  (M = Co and/or Fe) was obtained via the solvothermal method. Subsequently, the obtained  $KMF_3$  underwent treatment with a KOH aqueous solution, leading to the formation of a hydroxide shell on its surface. The next step involved rinsing the intermediate with water to remove any unreacted  $KMF_3$ , resulting in the formation of hollow nanoparticles of metal hydroxides. We controlled the metal ratio of cobalt and

iron in the metal hydroxide hollow nanoparticles by employing  $\text{KCo}_{1-x}\text{Fe}_x\text{F}_3$  where  $x = 0, 1/4, 1/2, 1$ . Such compositional variance has the potential to impact OER catalytic activity significantly. In the presentation, the formation of the structure will be elucidated, including the effects of varying Co/Fe ratios.

**Reference:** [1] M. Chauhan, S. Deka, *ACS Appl. Energy Mater.* 2020, **3**, 977; [2] D. S. Patil *et al.*, *J. Electroanal. Chem.*, 2020, **862**, 114012.

## Development of Chiral Mesoporous Gold Films for Chiral Discrimination

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Chirality is the property of a three-dimensional object or phenomenon that cannot be superimposed on its mirror image, which appears in many molecules and is also important for understanding its physical aspects. Chiral drugs have different pharmacological effects depending on their enantiomers: (R)-thalidomide exhibits hypnotic sedative properties, while (S)-thalidomide exhibits teratogenic properties. Therefore, for safe drug use, it is important to developing the methods and tools that enable discrimination between enantiomers.

Chiral discrimination based on optical measurement is generally performed using a conventional circular dichroism (CD) spectrophotometer or polarimeter. However, these methods tend to require a certain amount of sample for accurate measurement due to their relatively low sensitivity in some cases. This is because the "light-molecule interaction" is weak due to the difference between the spatial scales of the light and the molecules to be analyzed. Circularly polarized light is a helical electromagnetic field with a pitch of several hundred nanometers, so it does not interact sufficiently with chiral molecules with a size of several nanometers, and chirality cannot be sensed upon irradiation [1].

In this study, we develop a chiral mesoporous gold films which exhibit CD. At mesoporous gold films [2,3] consisting of numerous molecular-sized pores, an intense electric field matching molecular size is induced within their nanopores. We believe that chirality can be imparted to the strong electric field by designing nanostructures with chirality and/or CD.

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## Electroless Deposition of Mesoporous Metal Films by Displacement Plating

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Metals, especially noble metals, have various applications such as catalysts and electrodes. Since noble metals are expensive, research on porous metals has been conducted to expand the specific surface area. Mesoporous metals, which are formed by using molecular assemblies of amphiphilic materials as a template, are attractive because of their unique porous structures. They can incorporate relatively large chemical species into the pores. Also, they show good diffusion behavior of various chemical species. Therefore, various applications have been proposed. Mesoporous metals can be formed as films, which are advantageous in device applications such as sensors. Electrolytic plating has conventionally been used for the preparation of mesoporous metal thin films.<sup>1)</sup> However, electrolytic plating has some drawbacks. Uniform film formation on non-flat substrates is difficult due to uneven electric field strength. Also, it is difficult to form uniform films over a large area due to voltage drop. In addition, this method requires electricity and special instruments. If mesoporous metal thin films can be formed without electrolysis, above problems can be solved. Here, we report electroless deposition of mesoporous metal films by displacement plating. It is a reaction on a metal substrate in a solution containing ions of a metal, whose ionization tendency is lower than that of the metal of the substrates. When metal substrates are kept in the solution, the metal of substrates is dissolved by oxidation and metal ions of the solution are deposited by reduction.

We used PMMA<sub>150</sub>-b-PEO<sub>114</sub> as a template<sup>2)</sup> and investigated the preparation of mesoporous platinum and palladium films using K<sub>2</sub>PtCl<sub>4</sub> and K<sub>2</sub>PdCl<sub>4</sub> as the metal precursors. We used Sn, Ag and Cu as a substrate. PMMA<sub>150</sub>-b-PEO<sub>114</sub> was dissolved in THF, and hydrochloric acid, the aqueous solution of the metal precursors was added to prepare the reactant solution. The substrates are kept in the reactant solution at room temperature for the preparation of the mesoporous films of Pt and Pd. Finally, the film was washed with a 1:1 mixture of THF and water. By SEM observation, we confirmed regularly arranged mesopores with a diameter of ~10nm in the thin films. The metals in the reactant solution were found in the films using EDS. When we use a noble metal (Au) or a nonmetal (Si, SiO<sub>2</sub>) as a substrate, we didn't confirm the formation of the mesoporous metal films. Thus, it was shown that the mesoporous metal thin films were formed by displacement plating. With this method, problems of electrolytic plating are solved, and mesoporous metal thin films would be formed on substrates with various shapes such as powders and fibers.

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## Mesoporous Gold Electrodes Modified with Peptide Nucleic Acid for Detecting MicroRNA

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MicroRNAs, which are non-coding RNAs of approximately 20 nucleotides in length that regulate translation of messenger RNAs into proteins, have recently attracted attention as potential biomarkers because circulating microRNAs secreted into body fluids have been shown altered expression profiles depending on various diseases including cancer [1].

To establish a standard detection technique for practical application of microRNA as a biomarker, various detection methods based on electrochemical, electric, and optical methods have been newly proposed, as well as improvements in conventional methods including qRT-PCR, microarrays, and next-generation sequencers. Among them, electrochemical methods have gained attention due to their advantages of high sensitivity, shorter time to results, and ease of miniaturization [2], which are essential to point-of-care devices. In electrochemical detection of microRNAs, a lot of studies have demonstrated that the use of

nanostructured substrates, such as mesoporous thin films [3], and the surface modification with immobilized capture probes, including complementary DNA or peptide nucleic acid (PNA) [4], result in the improvement of its sensitivity and specificity, respectively.

In this study, we focused on the preparation of electrodes with combining (1) mesoporous gold substrates and (2) capture probes based on PNA, which has no electrostatic charge on its main strand unlike DNA, aiming at the improvement of both sensitivity and specificity in the electrochemical detection of microRNA. By using the ferrocyanide/ferricyanide redox couple as an indicator, electrochemical measurements including differential pulse voltammetry and cyclic voltammetry are carried out for the electrodes before and after incubation with aqueous solution containing microRNA. To consider the optimum combination of nanostructures and surface modifications for future optimization of electrode design combining nanostructures and surface modifications, the effects of differences in PNA probes as well as surface structures of gold electrodes are examined.

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## Synthesis and Characterization of Nickel Cobalt Glycerate Derived Nickel Cobalt Based Metal-Organic Framework

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This study produced Ni/CO-MOF material from Ni/Co-Glycerate with Ni:Co composition ratios of 1:2, 1:5, and 1:10. The Ni/Co-Glycerate template was synthesized using the solvothermal method at 180°C for 16 hours and dried at 60°C for 6 hours. MOFs were synthesized by dissolving Ni/Co-Glycerate as the metal ion source and 2-mIM as the ligand in distilled water at room temperature. The participant was washed with ethanol and dried for 16 hours at 80°C. X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Fourier-Transform Infrared (FT-IR) were used to examine material properties. The XRD results show that increasing the concentration of nickel metal can increase crystallinity, according to increasing intensity peaks at  $2\theta$  of 7.19°, 10.30°, 12.39°, and 17.88°. The morphology of Cu/Ni-MOF is hybrid; the hydroxide phase has a flower-like morphology, and MOFs have a circular shape. The similarity of the peaks indicates that the functional groups in the Ni/Co-MOF material are the same at different metal concentrations.

## A Theoretical Investigation on Nitrogen Dioxide Adsorption on Self-Assembled Monolayer-Functionalized ZnO Monolayer

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This study employs Density Functional Theory (DFT) calculations to elucidate the adsorption mechanism in the context of a ZnO monolayer system integrated with a Self-Assembled Monolayer (SAM) for NO<sub>2</sub> detection. Through rigorous computational analysis, we delve into the intricate interplay of geometric transformations, the dissociation of NO<sub>2</sub> bonds, and shifts in electronic properties ensuing from the introduction of the SAM. The observed modifications underscore the pronounced influence exerted by the SAM on the system's behaviour. This investigation not only sheds light on the underlying mechanisms but also paves the way for potential experimental applications involving the functionalization of ZnO with SAM for enhanced gas sensing performance. The findings hold significant promise for the advancement of gas sensor technologies with improved sensitivity and selectivity.

## Synthesis and Characterization of ZIF 67 Mangan Bimetal for Electrochemical Sensor Application

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The field of sensor applications has witnessed substantial growth in diverse domains, including agriculture, food, oil, environment, and medicine. Among the varied methodologies employed, electrochemical methods stand out. The judicious selection of appropriate materials in this context significantly augments sensor efficiency. Zeolitic Imidazolate Framework 67 (ZIF 67), a porous and highly porous material with an expansive surface area, offers facile synthesis, yet is impeded by limited conductivity. The introduction of additional metal derivatives has been reported to enhance its conductivity, with manganese, a transition metal, identified for its potential conductivity improvement and its influence on particle size. Thus, this paper aims to comprehensively explore the properties of Mn-modified ZIF 67, spanning structural, morphological, and electrochemical properties. Research findings indicate that Mn doping enhances crystallinity, as evident from X-ray diffraction analysis, while also impacting particle size (from  $\bar{x}$  514.4 nm to 944 nm), as assessed through SEM measurements. Furthermore, electrochemical performance reveals heightened peak current during redox processes, indicative of improved conductivity. In light of these outcomes, this material emerges as a promising candidate for electrochemical sensor development.

## Preparation and Properties of Bimetallic Co/Cu ZIF-67 for Electrochemical Application

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Efforts to enhance the electrochemical properties of materials have become the focus of numerous studies because these properties are essential in various fields of application. Zeolitic imidazole framework-67 (ZIF-67) is a type of metal-organic framework (MOFs) expected to demonstrate excellent performance in electrochemical applications due to its numerous distinct properties. Consequently, various strategies and techniques have been developed to improve the electrochemical performance of ZIF-67. In this study, we employed bimetallic ZIF-67 constructed with cobalt (Co) and copper (Cu) metal ions within the imidazole frameworks. The use of bimetal is expected to increase conductivity and fine-tune the physicochemical properties of ZIF-67. Using coprecipitation methods, we synthesized both single-metal and bimetallic ZIF-67 and compared their characterizations. The addition of Cu metal ions does not alter the materials phase, ensuring compatibility with the single-metal ZIF-67 structure. However, the rhombic dodecahedron morphology of ZIF-67 shifts from a smooth to a concave and rough surface in Co/Cu ZIF-67. Furthermore, Co/Cu ZIF-67 exhibits higher peak current on their cyclic voltammetry (CV) curve. The results effectively illustrate the advantages of bimetal on ZIF-67 properties and performance. Finally, this study successfully briefly demonstrate the potential development of Co/Cu-based ZIF-67 for various electrochemical applications.

## Facile Preparation and Characterization of Metal Phosphate for Battery-like Supercapacitor

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In this study, nickel cobalt phosphate ((Ni,Co)(PO<sub>4</sub>)<sub>3</sub>) has been developed as a positive electrode in supercapacitors. (Ni,Co)(PO<sub>4</sub>)<sub>3</sub> is synthesized through a phosphorization and carbonization method using



NiCo glycerate as a precursor combined with triethyl phosphate (TEP), subsequently an annealing process at 600°C under air conditions. The choice of solvent like hexanol has a significant influences on the morphology of nickel cobalt phosphate ((Ni,Co)(PO<sub>4</sub>)<sub>3</sub>), leading to the formation of cracker-like structures. Additionally, the resulting product exhibits an amorphous phase, indicating the absence of a well-defined crystalline arrangement. The electrochemical performance evaluation shows the peak from oxidation and reduction reactions at scan rate 5 mVs<sup>-1</sup> until 100 mVs<sup>-1</sup>. Following that the specific capacitance reaches 743 Fg<sup>-1</sup> at current density 1 Ag<sup>-1</sup>.

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