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ABSTRACT BOOK

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Session: JST-ERATO Special Session: Australian Science and Technology (Broadcasting to the JST-ERATO Center Venue)

Multi-Colour Synergistic, Antagonistic and Orthogonal Photochemistry for Macromolecular Synthesis

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The development and understanding of both covalent bond formation as well as dissociation remains a grand challenge in the design of photodynamic material systems. Initially, the lecture will dive into the photophysics of a range of reaction systems devised in our laboratories, exploring how their chemical response varies as a function of varying monochromatic wavelengths, establishing synergistic, antagonistic and orthogonal reactions modes. Surprisingly, the absorption spectrum is a poor indicator for photochemical reactivity, as will be demonstrated by a range of action plots on different reaction systems.

Based on the in-depth insights of our action plot analyses, we will explore how the light-responsive adaptation of polymer materials requires specific wavelengths to induce reversible covalent bond formation and dissociation. Our efforts have been devoted to pioneering a toolbox of photocycloadditions that can be triggered by lower energy visible light, while their cycloreversion functions at the least energetic wavelength, too. The lecture will showcase the latest applications of reversible photochemistry for the generation of light adaptive nano- and micro-structured materials, including examples of out-of-equilibrium photo-dynamic soft matter materials and dual-colour responsive inks for 3D laser lithography. Examples of irreversible photochemical system for wavelength orthogonal materials designed will be additionally highlighted.

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Assembly and Reaction of Molecular Fluids Undergoing Flow

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Determining the viscosity of a fluid has been of interest since molecule dynamics simulations first became possible, with structure-property relationships being able to be simulated under extreme conditions not easily accessible in the laboratory. The results have been of considerable interest to the polymer and petroleum industries. Non-Newtonian fluids, where the viscosity changes with the flow rate, have been of particular interest. However, these calculations are non-trivial, with care required to ensure that artefacts are not introduced by the simulation methodology. In addition, different techniques must be introduced to look at nanoconfined systems and bulk systems.1,2 Beyond viscosity, interesting phenomena such as flow-induced alignment self-assembly, stick and slip at wall boundaries, and mechanochemistry can also be studied. Computational resources and algorithms are now becoming available to study these types of behaviour, and some algorithms have been integrated into popular software packages.

Recently, we have been looking at improving the speed and accuracy of these implementations.

In this talk, some of the challenges for study of these types of system are presented. In addition, our results from studies of self-assembly of small nanoparticles, controlling slip past graphene interfaces with functionalization, and mechanochemistry under different types of flow will be discussed.

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Nanostructured Materals for Electrocatalytic Refinery

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Compared to modern fossil fuel-based industrial refineries, the emerging electrocatalytic refinery (e-refinery) is a more sustainable and environmentally benign strategy to convert renewable feedstocks and energy sources to transportable fuels and value-added chemicals. E-refinery promisingly leads to defossilization, decarbonization, and decentralization of chemical industry. Specifically, powered by renewable electricity (e.g., solar, wind and hydro power), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) can efficiently split water into green hydrogen, CO_2 reduction reaction (CRR) can convert CO_2 emissions to transportable fuels and commodity chemicals, and N_2 reduction reaction (NRR) can potentially manufacture fertilizers at ambient conditions.

A crucial step in realizing this prospect is the knowledge-guided design of appropriate reactions and optimal electrocatalysts with high activity and selectivity for anticipated reaction pathways, which dominantly involve cleavage and formation of chemical bonds between H, O, C, and N. In this presentation, I will talk about our recent progress in mechanism understanding and material innovation for a series of crucial electrocatalytic reactions (OER, HER, CRR, NRR, etc.), which are achieved by combining atomic-level material engineering, electrochemical evaluation, theoretical computations, and advanced *in situ* characterizations. A special emphasis is placed on the rational exploration of novel single-atom catalysts. I will also demonstrate the framework and methodologies of e-refinery with greater complexity by electrocatalytic coupling *in situ* generated intermediates (integrated reactions) or products (tandem reactions). It will inspire and accelerate further investigations of e-refinery to complement or displace some important industrial processes, and ultimately make the energy and chemical sectors sustainable.

Harnessing Solar Energy through Catalysis to Make Chemical and Fuel

Rose Amal

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Catalysis is the heart of chemistry – most chemical reactions need catalysts – so we want to make these reactions efficient and the process as sustainable as possible. Turning to the Sun as an energy source to activate catalysts is an obvious place to focus our investigations because it reduces our reliance on unsustainable fossil fuels. There are a number of means in utilising the sun's energy to drive energetically demanding catalytic processes. We can use (i) electricity from photovoltaic transformation of sunlight to drive electro-catalytic reactions (electrocatalysis), (ii) heat of the sun to activate thermal catalyst (thermal catalysis), and (iii) light of the sun to excite electrons from valence band of a semiconductor to its conduction band (photo catalysis).

Here, I present our ongoing research in harnessing the full solar energy spectrum (from ultraviolet to infra-red) to induce or/and enhance catalytic CO_2 and NOx reduction. Using solar energy to catalytically reduce CO_2 and NOx has the potential to convert the waste CO_2 and NOx into fuel and feedstocks, allowing the dual opportunity to store the intermittent renewable energy as well as closing the anthropogenic carbon and NOx cycle.

Electrochemical Manufacturing: Where are We Now?

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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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3D-Printed and Surface Metallized Plastic Waveguides for sub-THz Communications

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Applications of submillimeter and THz electromagnetic (EM) waves from 100 GHz to 1 THz are expanding in communications (beyond 5G and 6G), security, and sensors. In this frequency band, metal waveguides are commonly used as transmission channels to confine EM waves inside metal waveguides, but the size of the waveguide needs to be sub-millimeter, and the cross-section size of H-band (220GHz–325GHz) waveguides is standardized to be 864 μm x 432 μm, which is difficult to achieve by conventional metal machining processes. This difficulty becomes more apparent the higher the frequency. One way to solve this is to utilize 3D printers [1]. 3D printers can be either metal 3D printers or UV-cured resin 3D printers for sub-THz range applications. Although the former can directly form metallic waveguides, it is difficult to fabricate structures with a resolution of several tens of microns and control the surface roughness of the formed

structure. On the other hand, UV-curable resin type 3D printers are capable of fabricating structures with relatively high resolution and flat surfaces. However, while previous UV-curable resin type printers have been able to fabricate structures with a resolution of about 100 μm, and it has been difficult for conventional UV-curable resin type 3D printers to achieve resolution of 20 to 30 μm. To solve this problem, we developed a new UV-curable resin type 3D printer, RECILS [2]. RECILS has a unique structure employing a cylindrical window and this structure realizes the high resolution of 20 to 30 μm. However, to confine EM waves in the fabricated structure, the surface of plastic waveguide must be plated with metal. The hybrid technology using RECILS and metal plating will create a new market of sub-THz waveguide devices.

We fabricated H-band plastic straight waveguide using RECILS and metal plating. Waveguides have a cross section of 860 μm and 430 μm and a length of 1 inch (25.4mm). Insertion losses of fabricated waveguides were evaluated and confirmed that these plastic waveguides show insertion loss of less than -1 dB in the range of H-band which is equivalent to commercial metal waveguides.

Considering the increase in frequency of EM waves in the future, the hybrid technology is a very attractive candidate for making functional waveguides such as directional couplers, band pass filters, corrugated horn antennas and phased array antennas consisting of multiple waveguides arranged in three dimensions in the submillimeter and THz wave range. In addition to these features, the hybrid technology is expected to give designers of EM devices more freedom to create new devices. The use of RECILS is also expected to lead to new developments in waveguide devices for satellite applications by taking advantage of its lightweight feature. It is also worth mentioning that manufacturing costs are low.

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Additive Manufacturing of Advanced Materials

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Additive manufacturing is a transformative approach that uses direct deposition of materials to yield value-added products. New functional materials compatible with these emerging processes are required to enable smart surfaces and objects with seamlessly integrated sensing and responsive capabilities. To ensure compatibility, materials innovation must be carried out in parallel with the development of evolving manufacturing methods. Key to advanced manufacturing is the creation of carefully designed material packages specifically conceived to function with additive manufacturing. 2D printing is an additive manufacturing process that provides unique advantages such as manufacturing on flexible substrates in large-areas with high throughput. Steady progress in 2D printed electronics has led to improvements in device performances and has increasingly

impacted interactive display technologies, effectively enhancing the human-machine interface. However, the demands to provide increasingly complex, conformal, and stretchable electronics with more diverse functionality is pushing the development of a new generation of printable materials. One emerging opportunity is in-mold electronics, a fabrication methodology that relies on 2D printed electronics that can be molded into any shape using thermoforming. Thus, with suitable materials, in-mold electronics provides a strategy to generate adaptive and sensing conformal surface using additive manufacturing methods and thus enhancing the interactive experience in automotive, aerospace and household applications. But, we live in a 3D world and thus there is a push to produce smart 3D objects directly. To make smart 3D object directly, what we need are smart materials, where we can exploit fundamental concepts in chemistry/physics, such as self-assembly, to spatially structure multiple and distinct materials over multiple length scales. Through novel chemistries, and the exploitation of controlled self-assembly, various functions (e.g. electrical, optical, magnetic, mechanical) may be introduced into objects as they are being printed. With this level of control, adaptive, interactive, intelligent parts can be 3D printed that will support the next generation of objects for industries including automotive, manufacturing, healthcare and consumer goods.

In this talk, I will be presenting materials developed for 2D additive manufacturing such as silver and copper molecular inks for electronic applications and a novel strategy to generate functional and structural objects by vat polymerization 3D additive manufacturing that relies on controlled phase separation. Using photoresins comprising of judiciously selected components, the diffusion of phase separating components are modulated via the kinetics of gelation and network entrapment to yield spatial control over material placement. This strategy is an example illustrating a promising way forward in the integration of dissimilar materials in 3D printing of smart or functional objects such as sensors and wireless applications.

Near Unity Anti-Stokes Photoluminescence Quantum Efficiency from $CsPbBr_3$ Perovskite Quantum Dots Embedded in a Cs_4PbBr_6 Crystal

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In recent years, metal halide perovskites have attracted significant attention as novel semiconductors materials for next-generation solar cells and light-emitting devices. Due to their defect tolerance nature, halide perovskites have excellent optoelectronic properties such as long carrier lifetime and high photoluminescence (PL) efficiency. Also, halide perovskites have strong electron-phonon interactions [1-3], which are far different from conventional semiconductors. The high PL efficiency and the strong electron-phonon interactions lead to efficient anti-Stokes PL, which is higher-energy emission than the excitation light. If the anti-Stokes PL efficiency is sufficient, the material loses its energy and is cooled down by continuous photoexcitation. That is, optical cooling is realized. On the other hand, it has been challenging to maintain the high PL efficiency in halide perovskites because this class of materials is easily degraded by air exposure and light irradiation.

We recently reported intense anti-Stokes PL from $CsPbBr_3$ perovskite quantum dots embedded in a Cs_4PbBr_6 crystal [2]. Since the quantum dots are protected by the host crystal, the PL efficiency

is highly stable compared with their bulk counterpart. We demonstrate that the phonon-assisted process dominates the Urbach tail of optical absorption and anti-Stokes PL at room temperature. Based on the detailed analysis of the band-edge PL spectra, we demonstrate that external PL quantum efficiency of more than 97% is required to achieve optical refrigeration in this material. On the other hand, we have successfully fabricated samples with an external quantum efficiency of over 97% at room temperature. Furthermore, anti-Stokes PL is observed down to 70 K. These results indicate that this material has a high potential for optical refrigeration.

In the presentation, we will show the detailed experimental data and the theoretical background of semiconductor optical refrigeration.

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Characterization of SiC Formed at Various Locations in the Acheson Process

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In order to understand the formation of silicon carbide (SiC) in the Acheson process, a hot model study of SiC formation was carried out at a laboratory scale. Silica sand and carbon powder were used as the raw materials, and electrode temperature was maintained constant in a 20kgs capacity heat resistance furnace. The product samples were collected from the furnace's various radial and angular directions. Characterisation of the product/s was done using XRD and SEM techniques. SEM results reveal an interesting morphology of the formation of SiC, and XRD shows the various phases present in the sample. The product morphology and various phases present in it change significantly as one moves away from the electrode surface.

Understanding the Dynamics of Precursor Gases for the Growth of Doped Diamond: Pulsed Gas Injection Study via Optical Emission Spectroscopy Analysis

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Electronic components (e.g. transistors) based on synthetic diamond can offer a wide range of advantageous characteristics to various electronic devices due to exceptional properties of diamond. Synthetic diamond is usually fabricated via Microwave Plasma Enhanced Chemical Vapor (MW PECVD) process using various gas precursors (such as hydrogen, methane, etc.). Recent studies have highlighted that the enhancement of dopant incorporation (i.e. phosphorus)

can be achieved using pulsed gas injection method [1,2]. In this connection, it is important to understand the dynamics of precursor gases to facilitate a more efficient phosphorus doping of diamond, which would contribute to the development of the next generation power electronic applications.

Here, the dynamic response of different gases (nitrogen, methane, and oxygen) impulse in hydrogen plasma is studied in two different diamond growth reactors (MW PECVD type). These reactors are of different volumes and operate at various process parameters (e.g. pressure and total gas flow). The time responses to the precursor gas injection are recorded by Optical Emission Spectroscopy (OES) method [3].

Experimental time responses are fitted using an impulse response equation [3]. The analysis of the extracted fitting parameters gives important data on the precursor species' residency period as a function of different synthesis parameters. We show, that total gas flow, process pressure, and volume of the growth reactor are crucial for the optimization of phosphorus doping of diamond using pulsed gas conditions. Obtained fitting parameters can be used to predict the evolution of precursor species' concentration in MW PECVD reactors in the presence of intermittent gas flows.

This work was supported via the Czech Science Foundation grant GACR 21-03538S, the SGS Student Grant SGS22/161/OHK3/3T/13, and and the Operational Program Research, Development, and Education financed by European Structural and Investment Funds and the Czech Ministry of Education, Youth and Sports (projects SOLID21—CZ.02.1.01/0.0/0.0/16_019/0000760)

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Session: UQ-ITB Special Session

Modified Metal Organic Frameworks as Highly Sensitive Biomarkers for Detection of Viruses and Cancers

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Public awareness on high health quality increased year by year especially since the outbreak of Covid-19. The public demand on rapid detection also increased making the research on rapid detection or point of care device also increased in the last three years. As a contribution, our laboratory has developed various metal organic frameworks and their modification as a matrix for biosensor either for virus detection or cancer marker detection. For COVID-19 detection, UiO-66 modified gold SPR chip has been prepared to detect receptor binding domain of SARS-CoV-2 by SPR technique. The UiO-66/scFv functionalized chip is capable to distinguish the infected samples from human nasopharyngeal swabs. The SPR sensors can achieve the lowest LOD of 0.1762 ng/mL or 1.762 x 105 virus/mL, comparable to the value of practical diagnostic tools for screening SARS-CoV-2 patients. Furthermore, UiO-66-NH_2 modified chip SPR is also utilized to detect breast cancer biomarker. The MOFs display a linear range detection of HBsAg from 1-40 ng/ml with a limit of detection of 0.288 ng/mL. Amorphous HKUST-1 has been prepared by employing high concentration of triethanolamine during co-precipitation process. The spherical particles in nanoscale were formed and the amorphous structure was proven by X-ray Diffraction. In addition immersing the nanoparticles in water was found to change the amorphous HKUST-1 to crystalline $Cu(OH)_2$ nanosheets. As a dengue virus immunosensor, both products possess relatively high sensitivity with limit of detection being 1.60 pg/mL and 2 pg/mL, respectively. Moreover, one dimensional of HKUST-1 minirods were also obtained by controlling the amount of triethanolamine involved during preparation. With minirod structure the limit of detection of 12 pg/mL was achieved. Bimetallic HKUST-1 was also prepared by adding nickel precursor in the prepared solution. The proper ratio of Cu:Ni resulted in the low detection limit down to 0.77 pg/mL. Copper based MOF was also prepared as a matrix for Hepatitis B immunosensor. The sphere structure of MOF displays high sensitivity with detection limit of 730 pg/mL following with high stability and selectivity. The Cu based MOFs were also used to support point of care device for early detection of Hepatitis B. The device can detect HBsAg at low concentration as low as 0.868 pg/mL.

Transparent NIR absorbing films for photothermal application

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Photothermal (PT) materials that generate thermal energy by absorbing near-infrared (NIR) rays are of strong interest in PT therapy, optical sensors, and soft robotics. Especially, the photo-actuator, which induces mechanical changes through light, is wireless, but its movement can be highly controlled depending on the wavelength and intensity of the light. Most of the materials with strong absorption in the NIR region have absorption peaks even in the visible region, so their color is dark, and their utility is low, making it difficult to study. Herein, we introduce a transparent NIR dye that strongly absorbs NIR light while transmitting almost all visible light (%T > 90%). The NIR dye was widely and evenly dispersed in the transparent polymer binder, resulting in a clear film without turbidity. This NIR absorbing film absorbed light at 1064 nm, converting most of its energy into thermal energy (Photothermal efficiency>75%). Based on its high photothermal conversion efficiency, the NIR absorbing film has confirmed its applicability for desalination of brine. A double-layered photoactuator was made by layering PDMS on the film,

and the movement of the transparent photoactuator according to light control was confirmed. The mechanisms of photothermal effect and application potential of the NIR absorbing film will be discussed.

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General Fabrication of Metal-Organic Framework-Derived Porous Metal-Doped Cobalt Oxide Nanosheets for Ammonia Sensing

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Metal-organic frameworks (MOFs) have gained significant attention as precursors or templates for the derivation of various porous materials, including porous carbons, metal oxides, metal chalcogenides, and metal carbides due to their tunable composition and pore size and large surface area.[1-3] However, the derived porous materials typically assume the inherent morphology of the parent MOFs, thus limiting the control over their final morphology. This work demonstrates a general strategy for preparing a series of mesoporous two-dimensional (2D) metal-doped Co_3O_4 nanosheets using benzene tricarboxylic acid-based MOFs as templates/precursors, including Cu-BTC, Co-BTC, MOF-808 and Fe-BTC by exchange reactions in aqueous cobalt-containing imidazolate solution followed by calcination in air at 300 °C. The resulting 2D metal-doped Co_3O_4 nanosheets exhibit a narrow pore size distribution in the range of 2-10 nm. More importantly, the pore size distribution can be controlled by adjusting the calcination temperature of the precursor nanosheets. When employed for ammonia sensing by quartz crystal microbalance (QCM) technique, the Fe-doped mesoporous Co_3O_4 nanosheets shows the highest response toward ammonia (10 ppm) with a high frequency change of 1699 Hz, which is 2.8, 14.4- and 5.8-times than the response of Zr-doped Co_3O_4, Cu-doped Co_3O_4, and pure Co_3O_4, respectively. Furthermore, the Fe-doped mesoporous Co_3O_4 nanosheets can selectively detect NH_3 gas with a high selectivity of 48% in the presence of other interfering compounds, such as aniline, triethylamine, ethanol, acetic acid, acetone, benzene, formaldehyde, formic acid, carbon

tetrachloride and water. These nanosheets exhibit an outstanding limit of detection of 59 ppb and good long-term stability with stable responses over a period of 180 days. The adsorption of NH_3 on the Fe-doped mesoporous Co_3O_4 nanosheets arises from the reversible interaction between the ammonia molecules and the OH groups of the surface of these nanosheets In addition, the presence of metallic Fe remarkably enhances the sensing activity because of the chemical sensitization mechanism, since the heterostructure can offer not only efficient electron transfer and abundant active adsorption centers for the incoming gas molecules, but also helps the spillover of oxygen species onto the Co_3O_4 surface, where they get ionosorbed by trapping electrons from Co_3O_4 (dipole-dipole interaction with the oxygen surface of Co_3O_4). The presented strategy will be useful for future design and construction of metal-doped mesoporous oxide nanosheets for gas-sensing and other applications.

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Modification of HKUST-1 for Highly Sensitive DENV-3 Immunosensor

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In this work, the amorphous HKUST-1 nanoparticles and copper hydroxide ($Cu(OH)_2$) nanosheet were successfully prepared by involving diethanolamine (DEOA) as modulator and were applied as an immunosensor to detect dengue virus (DENV-3) NS1. The synthesized method used co-precipitation with distilled water as solvent and was controlled by adding 35 wt% of DEOA. This modulation controlled was found not only can provide a base environment, but also act as a crystal modifier for the HKUST-1 structure. The DEOA changes the crystallinity and morphology of HKUST-1 into amorphous and highly uniform nanoparticles, respectively. In addition, the $Cu(OH)_2$ nanosheet was also obtained by immersing the amorphous HKUST-1 in water for 6 hours. The crystallinity and morphologies of both aHKUST-1 and $Cu(OH)_2$ NS were analyzed using X-ray diffractometer and scanning electron microscopy, respectively. Then the infrared spectrum was recorded by Fourier transform infrared spectroscopy at the wavelength in range of 500-4500 cm^{-1} to analyze the chemical properties. The amorphous HKUST-1 nanoparticles (aHKUST1 NPs)

and $Cu(OH)_2$ nanosheet ($Cu(OH_2)$ NS) were functionalized as a matrix material to immobilize the DENV-3 monoclonal antibody. The immunosensor was fabricated by dropping the matrix on the surface of screen-printed carbon electrode (SPCE). The immunosensor performances were evaluated by employing cyclic voltammetry (CV), differential pulsed voltammetry (DPV), and electrochemical impedance spectroscopy (EIS) technique in detecting DENV-3 NS1 antigen at the analyte concentration in the range of 0.001 – 100 ng/mL. As immunosensor aHKUST1 NPs and $Cu(OH)_2$ NS can detect the antigen down to 1.64 pg/mL and 2.07 pg/mL, respectively. The amorphous nature of HKUST-1 is believed to provide many active sites that can enhance the electrocatalytic activities thereby improving the performance of the immunosensor. Inspiring by its high performance, further measurements which are selectivity, reproducibility, and stability were applied only on the electrode based on aHKUST1 NPs. The selectivity was observed by interfere immunosensor with other serotype of DENV to check the selectivity of aHKUST1 NPs to DENV-3. The reproducibility of immunosensor were checked in five electrodes that showed the good result. In addition to further investigate the performance of aHKUST1 as a DENV-3 immunosensor, the DENV-3 detection was carried out in human serum about 1 ng/mL, 10 ng/mL, and 100 ng/mL of DENV-3 antigen. The found antigen was approximated by dividing the current response to the antigen in PBS by the response to the antigen in human serum. Compared to the real concentration, the recovery values of each point are 98%, 94%, and 104%, respectively. In summary, based on all experiment showed that aHKUST1 has very potential to perform as excellent electrochemical immunosensor.

Mesoporous soft electronics: A novel approach towards biosensing and bioimplant applications

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Electronics that are both flexible and implantable show immense potential for use in more sophisticated medical applications, particularly in the monitoring and regulation of physiological brain activity. Miniature dimensions for spatial physiological mapping and low impedance for identifying tiny biopotential signals are two essential needs for neural interfaces. Both of these requirements must be met. For biosensing and bioimplant applications, we merge a bottom-up mesoporous deposition approach with a top-down microlithography procedure to build flexible and low-impedance mesoporous electrodes. The mesoporous designs that were generated as a consequence of a thin and soft polymeric substrate provide superior mechanical flexibility and robust electrical properties that are able to withstand numerous bending cycles. It is desirable to have high-density and high-resolution miniaturized electrode arrays placed over a soft, flat

substrate while attempting to understand the capabilities of complicated neuronal circuits. (1, 2) In order to permit the detection of relatively low biopotentials, which generally lie within a range of a few microvolts, implanted devices need to have a low impedance at the electronic-tissue interface. This is one of the essential requirements for implanted devices. (3, 4)The mesoporous network's large surface areas allow for a high current density in standard electrolytes, making it highly suitable for biological sensing applications. This suitability was demonstrated in glucose sensors, which had an excellent detection limit of 1.95 M and a high sensitivity of 6.1 $mA.cm^{-2}.M^{-1}$. This sensitivity was approximately six times higher than that of flat film-based devices. The as-synthesized mesoporous electrodes provide peripheral nerve recording features that have been successfully shown in vivo. These functions include a low impedance of less than 1 kΩ at 1 kHz in the electrodes, coupled with their mechanical flexibility and durability. The presence of these characteristics demonstrates that the innovative flexible nanoarchitectonics has the potential to be used in neural recording and modulation applications.

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Development of Metal-Organic Frameworks for Optical Biosensors

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The gold layer on the surface plasmon resonance (SPR) sensor chip is tough to detect small molecules without using specific receptors, one of which is the glucose molecule. However, metal-organic frameworks (MOFs) are helpful in biosensing technologies to help capture and co-localize enzymes and receptors with the target biomolecule. In many past studies, the properties of the MOFs are often ignored, with most studies focusing solely on selecting the appropriate receptors. One must also consider the technique and transducer used to take advantage of the MOFs' unique properties in sensors technology because these aspects will strongly influence the mechanisms that occur during the detection process. In this work, we have investigated the applications of MOFs for glucose detection without specific receptors using the SPR technique for the first time. Then, this work also seeks to improve its performance by modifying the MOFs with gold nanoparticles. The results show a high-performance SPR glucose sensor with a detection limit of 0.0693 mM (S/N = 3) in the concentration range of 0.01-10 mM. The selectivity test reveals that the UiO-66/Au-based SPR sensor exhibits a high selectivity toward glucose. Besides being used as receptors, MOFs also have the potential to be used as a single chain variable fragment (scFv)-based receptor matrix for the detection of SARS-CoV-2 because they have a large specific area and good adsorption ability. Our work successfully demonstrates its use in this regard. SPR chip with matrix MOFs developed can increase adsorption ability and support the one-to-one binding of scFv-SARS-CoV-2 recombinant binding domain (RBD). In addition, testing on SARS-CoV-2 infected nasopharyngeal samples from patients showed distinguishable responses between negative and positive samples. The resulting detection limit follows the standard screening tool for the detection of SARS-CoV-2, so it has the potential to be further developed.

Gold-Loaded Superparamagnetic Mesoporous Bimetallic CoFeB Amorphous Nanovehicle for Autoantibody Detection

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Non-noble metal-based mesoporous nanomaterials (MNs) fabricated by self-assembly of block copolymers have attracted enormous interest in a wide range of applications including catalysis, biosensors and energy, due to its high stability, specific surface area and flexible control of pore size/shape.[1-2] Therefore, building a well-defined mesoporous nanostructure using non-noble metals is crucial for their applications in biomedicine due to their highly expose active sites and accessible surfaces.[3] However, it is yet a great challenge to controllably synthesize superparamagnetic mesoporous nanospheres with tunable compositions and large pores, which are sought for immobilization or adsorption of guest molecules for magnetic capture, isolation, pre-concentration and purifications. We have developed a facile assembly strategy of block copolymer to fabricate exposed mesoporous CoFeB amorphous alloy with abundant metallic Co/Fe atoms, which can serve as an ideal scaffold for well-dispersed loading of Au nanoparticles (~3.1 nm) through the galvanic replacement reaction. The as-prepared Au-CoFeB possess a high saturation magnetization and uniformed open large mesopores (~12 nm), which give more opportunities and accessibilities to bulky molecules such as enzymes or antibodies. Through this unique combination of superparamagnetism (CoFeB) and bio-favorability (Au), the resulting Au-CoFeB is employed as dispersible nanovehicles for direct capture and isolation of p53 autoantibody from biological samples, allowing for highly sensitive detection of autoantibody with a limit of detection of 0.006 U/mL which is 50-times more sensitive than a conventional p53-ELISA kit-based detection system. The assay provides a rapid, low-cost, and portable platform with the potential to detect a wide range of other clinically relevant protein biomarkers. We envisage that this highly sensitive, rapid, and inexpensive assay could be useful in quantifying autoantibody and relevant biomarkers for various clinical applications.

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Palm Sugar-Induced Formation of Hexagonal Tungsten Oxide with Nanorods-Assembled Three-Dimensional Hierarchical Frameworks for Nitrogen Dioxide Sensing

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This work reports on the formation of a hierarchical three-dimensional (3D) structure assembled by nanorods of hexagonal tungsten oxide (WO_3) utilizing natural palm sugar as a structure directing agent. It was found that the concentration of palm sugar strongly affects the crystal structure and final morphology of WO_3 product. Higher concentration of palm sugar allowing the formation of monoclinic WO_3 with spherical morphology while lower concentration of palm sugar allowing the formation of hexagonal WO_3 with nanorods-assembled hierarchical 3D morphology. As a sensitive material for NO_2 gas sensor, the hexagonal WO_3 particles display a high response of 26 to 1 ppm of NO_2 at 250 °C. This oxide also shows a remarkable stability where the response retained stable over period of 24 days. In addition, selectivity test toward NO_2 against other gases such as CO, CO_2, SO_2, and NO shows that the oxide is highly selective to NO_2. The superior NO_2 sensing performance of these particles is attributed to the hierarchical 3D structure which can offer more adsorption sites for NO_2 molecules, while the assembling nanorods may provide more effective diffusion and transport for the NO_2 molecules. Further, the density functional theory (DFT) calculations reveal that NO_2 can gain more charge from hexagonal WO_3 than from monoclinic WO_3 upon adsorption, leading to a greater change in resistance.

Nanoengineered Glass-Grown Mesoporous Gold for Ultrasensitive Detection and Quantification of SARS-CoV-2

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Studying the effects of the seeding substrates (e.g., silicon, glass, etc.) on the growth dynamics of metallic films is crucial for preparing highly branched thin films with desired optical and electrical properties.[1] Understanding film growth (e.g., stress), the nature of substrates, and their successful characterization will allow for better insights into aspects of surface chemistry and reactions that influence the overall performance of the sensing device at each stage of preparation and readout.[2] Herein, we nanoengineered the mesoporous gold onto a glass substrate and demonstrate the attomolar (aM) detection of SARS-CoV-2. The mesoporous gold film grown on the glass substrate shows a preferential crystal growth on the <220> direction. The glass-grown mesoporous gold film experiences stress evolution throughout the thickness: where there are two microstructural forming processes: grain zipping and grain coarsening. Both processes lead to bigger grain size, which induces tensile strain by reducing the surface energy.[3] Furthermore, this film exhibits a

marked increase in crystallinity in every plane as opposed to the conventional silicon-grown gold film. As a result, fine structure attained from microstructural contributions serves as a sensitive metallic framework, leading to a short circuit pathway for dramatically accelerated diffusion and strengthening the point-of-care application in routine clinical practice for detecting infectious disease.

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Modification of Surface Plasmon Resonance (SPR) Biosensor using MoS_2-MoO_3 Hybrid Microflowers for CFP-10 Tuberculosis Detection

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Tuberculosis is a respiratory system disease caused by *Mycobacterium tuberculosis (Mtb)*. Tuberculosis has received special attention from every health institution due to overflow cases with a high mortality rate. Tuberculosis control involves multiple strategies and aspects, including developing rapid detection technology. Surface plasmon resonance (SPR)-based biosensor is a promising detection method because it has real-time detection features with competes performance. Stronger plasmon and higher bioreceptor absorption in sensor surfaces effectively enhance sensitivity and selectivity. MoS_2 owned the high optical absorption and large surface area, thus suitable for SPR biosensor modifier. In this study, the MoS_2-MoO_3 hybrid microflowers were developed to be applied in the SPR biosensor to detect the secretory protein of tuberculosis, CFP-10. The abundant edge active sites in microflowers morphology can support more bioreceptor absorption activity. The MoO_3 was used to overcome the MoS_2 drawback and enhance the SPR because of its oxygen vacancy. MoS_2-MoO_3 was synthesized by hydrothermal method with varied pH and trisodium citrate, which projected to influence the microflowers formation and size. The XRD and SEM characterization confirmed that MoS_2-MoO_3 hybrid microflowers were successfully synthesized with good morphology and small particle size from the hydrothermal at pH 7 with 0.5 g trisodium citrate. The deposition cycles of materials on the chip were varied, and it was observed that the thickness of MoS_2-MoO_3 influenced the sensors sensitivity. The SPR measurement given that the 12L chip provide optimum limit-of-detection of 3.45 ng/mL (S/N = 3.3) in the concentration range 62.5-500 ng/mL. The modified SPR chip provides ten times better performance than the bare chip. This biosensor also has good selectivity and reproducibility based

on measurement to other analytes and repeated measurements on five different chips. From this study, it has been proven that MoS_2-MoO_3 hybrid microflowers can significantly improve the performance of SPR biosensors. Therefore, this proposed SPR biosensor has the potential to be further developed and applied as a detection technology for CFP-10 in monitoring and diagnosing tuberculosis.

Hierarchical Porous Carbon Materials Derived from Nickel-Based Metal-Organic Framework with Coordinated Water for Adsorption Application

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Industrial dye is one of the most common toxins identified in wastewater. Both human health and the quality of the water can be significantly impacted by them. Therefore, the creation of improved adsorbents is urgently required for the quick and efficient removal of industrial dyes. Metal-organic frameworks (MOFs) are crystalline porous substances created by the coordination of metal centers/ions and organic ligands. The large surface area, tunable composition, controllable pore size, and abundance of metal active sites allow MOFs one of the most promising materials for wastewater treatment.[1,2] However, macromolecular dyes typically cannot pass through the microporous structure with small pore size, which weakens the MOF's ability to adsorb substances. Calcination to get porous carbon material is one of the efficiency methods for increasing pore size.[3,4,5] Here, we provide MOFs as novel templates for the synthesis of large-surface-area hierarchical porous carbon nanostructures that are useful for absorbing organic molecules. The conversion of adsorption capacity of hierarchical porous carbon material-Ni/C was prepared using fibrotic nickel benzenetricarboxylic acid MOF (Ni-BTC-F) precursors for the adsorption of methyl blue (MB). Ni-BTC-F, as opposed to standard Ni-BTC nanorods (Ni-BTC-O), have coordinated water in their structures, which aided in the development of mesopores after carbonization. The magnetism of Ni nanoparticles could be used to benefit the separation of Ni-MOF from the water. The coordination water in Ni-BTC-F was responsible richer pore size distribution for the Ni-BTC-F-Carbon, larger pore volume, and higher adsorption capacity, even though it had the same surface area as Ni-BTC-O-Carbon. In addition to the aforementioned advantages, Ni/C hierarchical porous carbon material, which was carbonized from Ni-BTC-F, had an outstanding adsorption rate. It could adsorb 80% of pollutants in one minute and attain 90% of its adsorption capacity for a 20 ppm MB solution in one hour, suggesting its potential as an MB adsorbent.

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Enlarging the Porosity of Metal-Organic Framework Derived Carbons for Supercapacitor Applications by Template-Free Ethylene Glycol Etching Method

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Metal-organic frameworks (MOFs) have gained significant attention as both carbon sources and self-templates for creating carbon materials with intrinsic porosity, tuneable composition and large surface area and pore volume. However, the preparation of hierarchical porous MOFs and the derived porous carbons have relied mostly on hard or soft templates. This work demonstrates a facile template-free etching strategy for enlarging the micropores in bimetallic zeolitic imidazolate framework (ZIF) particles into mesopores via an ethylene glycol-assisted aqueous etching method at room temperature. Hierarchical porous bimetallic zeolitic imidazolate framework (ZIF) particles (etched $Zn_{33}Co_{67}$-ZIF) exhibiting both micropores and mesopores have been successfully prepared while maintaining the framework integrity. The etching process effectively increases the pore size, surface area, and pore volume of the ZIF-based MOFs. After the thermal treatment, 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. When employed for supercapacitors, 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 mV s^{-1} than unetched bimetallic carbon ($Zn_{33}Co_{67}$-C) and Zn-only carbon (Zn-C), respectively. Furthermore, 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 facile template-free strategy to enlarge the porosity of MOFs, and their corresponding porous carbons and improve their energy storage performance.

Development of Copper-Nickel Based Metal-Organic Framework Material for Electrochemical Immunosensor Applications to Detect Dengue Virus NS-1 Serotype 3

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Dengue hemorrhagic fever (DHF) is the most common arboviral disease that is spread throughout

the world. This disease is caused by the dengue virus and infects humans through the bite of the *Aedes aegypti* mosquito. This disease is found in tropical and subtropical areas. In Indonesia, the prevalence of this disease is increasing every year. Early detection can be carried out so that the risk can be reduced. This study developed an electrochemical immunosensor based on a modified metal-organic framework (MOF) on the electrode surface to detect dengue virus NS-1 serotype 3. Cu-BTC and CuNi-BTC materials with variations in the Cu:Ni composition ratio of 5:1 (CuNi-BTC-1), 3:1 (CuNi-BTC-2), and 1:1 (CuNi-BTC-3), and the addition of 10 wt% triethanolamine (TEOA) as a modulator have been successfully synthesized. The synthesis was performed by co-precipitation at room temperature and dried at 60°C for ± 24 hours. Material characteristics were evaluated through several tests such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier-Transform Infrared (FTIR), Brunnauer-Emmet Teller (BET), and electrochemical testing. The performance of the material as an electrochemical immunosensor was tested using cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS).

The CV approach showed that CuNi-BTC-3 resulted in the optimum current for reduction of 19.12 A and oxidation of 13.17 A. Based on this result, CuNi-BTC-3 was used for electrochemical testing to detect dengue virus (DENV). The next process is detecting the dengue virus using the DPV approach in the linear range of NS-1 protein concentration of 5 $ngml^{-1}$ - 0.001 $ngml^{-1}$. The test informs that the CuNi-BTC-3 has the lowest detection limit or limit of detection (LoD) was 0.77 $pgml^{-1}$. The selectivity test on four variations of DENV serotypes showed that the CuNi-BTC MOF material had excellent selectivity against NS-1 DENV serotype 3. Serum test for NS-1 DENV serotype 3 with a concentration variation of 0.001; 0.01; 0.1; 1; and 10 ngml-1 resulted in recovery of 98%, 94%, 97%, 95% and 98%, respectively. The results showed the potential of an electrochemical immunosensor based on CuNi-BTC-3 material for detecting NS-1 DENV serotype 3 antigens.

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

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Two-dimensional metal-organic framework (2D MOF) nanostructures have attracted significant attention because of their ultrathin nature, high surface-to-volume ratio, and highly exposed active sites. This work describes the successful fabrication of hollow bimetallic nickel-cobalt benzene tricarboxylic acid (Ni-Co BTC) hexagonal nanoplates in the presence of polyvinylpyrrolidone (PVP) without the need for templates or etching. The adsorbed PVP molecules provide depletion forces between the nanoplates to prevent their aggregation and limit the vertical growth of MOF layers, allowing for 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 69.5 ppm of NH_3 vapor by quartz crystal microbalance technique. 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_3 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 promote hydrogen bonding with NH_3 molecules.

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Nanoarchitectured Superparamagnetic Iron Oxide-Doped Mesoporous Carbon Nanozymes for Biosensing Application

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The incorporation of nanoarchitectonics into the development of nanozymes to achieve target specific geometry, dense active sites, and cascade catalysis is highly demanded for developing ultrasensitive bioassay. The improved dispersion and uniform distribution of metal active sites onto a three-dimensional (3D) mesoporous carbon support (MC) with high surface area can lead to enhanced substrate binding, mobility, and collision probability and therefore, increased peroxidase mimetic activity. Herein, we report the fabrication of well-dispersed superparamagnetic iron oxide (IO) nanoparticles (NPs) on mesoporous carbon (IO-MC) support with high Fe^{3+} active sites, high surface area, and ordered mesoporous pore channels that show promising catalytic activity at room temperature. The as-prepared IO-MC shows good nanozyme activity at room temperature with highly favorable Michaelis-Menten constant, K_m (0.242 mM) and fast reaction rate (0.193×10^{-7} MS^{-1}). Finally, we demonstrate the functionality and pre-eminence of IO-MC nanozyme for bioassay. As a proof-of-concept, we develop a superior glucose assay that provide a LOD (limit of detection) of 2 µM in the spiked sample. These findings suggest that homogeneously dispersed iron oxide NPs on mesoporous carbon show great potential as next generation nanozyme for developing sensitive bioassays.

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