School of Chemistry

Senior Sophister Projects for Nanoscience, Physics & Chemistry of Advanced Materials 2020/21
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Inorganic and Synthetic Materials Chemistry
3D printing for catalysis

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Research Project Description:

Immobilising of heterogeneous catalysts is an important topic as it allows the benefits of selectivity with the ability to separate products from the catalyst. With the advent of 3D printing, some work has shown that heterogeneous catalysts can be printed [1], but there are no reports of a homogeneous catalyst being incorporated into 3D printed ‘reactionware’. In this project the aim is to immobilise a test catalyst – Wilkinsons Catalyst – into polycaprolactone that can be converted into filament for 3D printing. The advantages are that with the correct choice of polymer, the printing temperature will not decompose the catalyst; any shape reactionware module can be prepared; the reaction is on the solid-liquid interface, so this lends itself to microfluidics approaches where conventional techniques give high catalyst degradation and is the overall goal of this work.

The student will:

• prepare the catalyst,
• dope it into the polymer,
• convert this to a filament using in house equipment.
• Print reactionware using a 3D printer available for this project.
• Conduct test hydrosilylation reactions to evaluate the stability and recyclability of the catalyst.

In each step the catalyst will be characterised by solid-state $^{31}\text{P}$ NMR and thermal methods to ensure no oxidation or thermal decomposition of the catalyst. Wilkinsons catalyst is thermally stable to temperatures above the glass transition point of the polymer and has a convenient NMR probe. Once printed the catalyst will be used in the hydrosilylation reaction to evaluate the recyclability of the product and NMR spectroscopy will be used to see if the catalyst is leaching from the polymer.

References
Compound Interest: Heavy Metal Complexes as Photosensitisers

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Research Project Description: In general, the conversion of energy from one form to another flows downhill, with each step representing an energy loss. Upconversion is a mechanism by which carefully designed molecules can buck this trend by taking in light energy and pooling it so as to emit light of higher energy. This is a valuable phenomenon particularly in the development of next generation solar cells and photovoltaic devices and it has application in photocatalysis and luminescent oxygen sensing. The Draper team have uncovered the potential of some of their systems to engage in triplet-triplet annihilation, the molecular process at the heart of upconversion.¹

Triplet-triplet annihilation (TTA) works by taking a sensitizer (usually a transition metal complex (Ru(II), Pt(II) or Ir(III)) with accessible triplet excited states) to harvest the exciting light and to transfer the energy by triplet-triplet energy transfer (TTET) to an acceptor. The triplet excited state is annihilated by the collision of two molecules to generate one in the ground state and one in its singlet excited state. The radiative relaxation of the latter produces the upconverted fluorescence. Our work has centred on a series of symmetrical Ir(III) and Ru(II) 1,10-phenanthroline complexes (Figure 1) incorporating aryl acetylene chromophores of increasing size.

![Figure 1: Emission spectra showing the sensitizer emission alone (red) and upconverted emission from DPA (blue) in a donor acceptor mixture (*exciting at 473 nm)](image)

The aim of this project is to build on what is already known and to improve on these features in the next generation of triplet sensitizers.²³ The work forms part of on-going collaboration with Prof. Jianzhang Zhao’s research group at Dalian University of Technology. To date it has yielded some of the highest known upconversion quantum yields.

The project will involve ligand design and synthesis and the spectroscopic characterisation of the resulting novel metal coordination complexes. The materials will be screened in TCD for their optical properties and lead compounds will be sent to China for further testing with the hope of making further new contributions to the applications of the materials in Photodynamic Therapy and chemical transformations.

References
School of Chemistry Senior Sophister Research Projects 2020/21

When it Glows: Hybrid Coordination Complexes with Photoluminescent Functionalities

Prof. Sylvia Draper (SMD2)

Research Project Description: Coordination polymers with two kinds of connectors are of great interest owing to their various potential applications.\(^1\) Work within the Draper team has allowed for the formation of supramolecular coordination polymers using polypyridyl frameworks incorporating Cd(II), Sm(II), Ru(II), Fe(II) and heterometallic polymers based on Ag(I) and Ru(II). The research undertaken demonstrates the potential for π-stacking interactions to influence the crystal packing and supramolecular ordering in the solid-state. In a parallel research programme the Draper team has established a versatile route to fused luminescent poly(heteroaromatic)graphenes and polyphenylene.\(^2\) The aim now is to connect these two areas of research to produce novel heterometallic coordination polymers with intriguing and potentially exploitable photophysical properties.

Research Project: Coordination polymers derived from photoluminescent lanthanide(Ln) metal ions (Eu(III), Tb(III), Nd(III) etc.) show luminescence in the NIR region, which has a special significance in the area of sensors.\(^3\) Thus, binding the photoactive ML-fragment to Ln-based backbones in the proposed coordination polymers is expected to initiate definite changes due to energy transfer from the ML-fragment to the Ln-backbone. The plan is to prepare novel coordination complexes and coordination polymers with heterometallic centres based on a series of proposed ligands and to investigate the material properties of the emerging supramolecular array. The target is a set of fused polypyridyl materials with low lying π*-orbitals for near-IR absorption characteristics incorporating carboxyl groups for H-bonding interactions.

Methods/techniques: Synthetic activities will be undertaken within the host research laboratory and via the embedding of the student within the team. Metalloligands and coordination polymers will be characterized using various analytical techniques such as UV/vis absorption and emission spectroscopy, NMR, IR, ES-MS, and single crystal X-ray diffraction.

![Proposed Ligands](image)

Figure 1 Proposed Ligands for generation of metal-based photoluminescent polymers

References
Metal-based Molecular Switches Generated from Dithienyl Ethene (DTE)

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In recent years there has been a surge of interest in developing molecules that convert reversibly from one form to another on excitation with light.\(^1\) This is because when the forms of a photochromic material have different properties (e.g. fluorescence intensity, absorbance profiles) they can be exploited as “On” or “Off” states in a molecular memory, data storage or switching device.

Dithienylethenes (DTEs), first described by Irie\(^2\) and co-workers in 2000, have emerged as an important class of molecular switch, converting between open and closed forms (Figure 1). Most investigated are those comprising two 2,5-disubstituted thiophene units linked by a cyclopentene-derived bridge as these demonstrate high, thermal stabilities, fatigue resistance and cyclisation quantum yields.

**Objectives:** The concept of introducing a metal centre into the DTE motif is relatively recent.\(^3\) Our intention in this project is to contribute to this emerging field and to use metal coordination as an effective tool to lock certain organic conformations in place and to tap into metal-based states that will facilitate cyclisation via a different electronic pathway than that adopted by a purely organic material.

The group\(^3\) is currently working with Prof. F. Scandola an expert in the field and the project will involve organic synthesis, metal coordination chemistry, various characterisation tools, UV/Vis absorption and emission data and electrochemistry.

![Figure 1: The Open (colourless) and Closed (blue) of crystals of a novel molecular switch](image)

**References**

A Molecular Approach to Heteroatom-Nanographenes: tuning electronic behaviour with a synthetic chemist’s toolbox

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Products based on active thin-film organic devices are already in the market place e.g. as displays in mobile electronic appliances, however the future promises a radically new generation of ultra low-cost, lightweight, and flexible electronic devices if a carbon-based platform that can boast the necessary and discrete set of desirable properties and be found. Globally, there is a growing belief that graphene, the chemical focus of this project and heralded as the new material of the 21st century, could provide an answer to the emerging, translational and enabling nanotechnologies needed to replace silicon in the semiconductor industry. The problem is the absence of a band-gap in the pristine material.

Heteroatom doping is a promising approach for tuning the electronic properties of graphene, however current deposition methods for producing N-doped graphenes are unspecific (e.g. thermal evaporation of small organic moieties such as ethene and a nitrogen source (NH$_3$))

This project aims to address this deficit by developing a controlled and strategic approach to the deposition of fully characterized heteroatom graphene-like materials. This will be achieved using the N, S and P-doped polyphenylenes developed in the Draper team as feedstock. The work, facilitated by new and exciting collaborations between national and international groups, will allow a systematic and connected study of both solution and on-surface graphene development for the first time.

Figure 1 (a) Generation of N-doped graphene dimers via the thermal evaporation of precursors on Au (III) – Collaborator Prof. S. Decurtins

References:
Polycyclic aromatic hydrocarbons (PAHs) are important materials and by-products from the burning of carbonaceous fuels. Carbenoid examples include anthracene and pyrene and larger coronene systems such as hexa-peri-hexabenzocoronenes 1 (Figure 1), (HBCs). Their coordination chemistry can be explored by incorporating heteroatoms into their periphery \(^{(2)}\) but they also have untapped potential as organo-ligands and very few have been used to incorporate -bonded metal centres. The aim of this project is to generate a new set of metal-organics with interesting and tunable photophysical and chemical properties. Such compounds are molecular models of metal-intercalated graphitic sheets and commonly used catalysts, such as dispersed Pd on graphite.

![Figure 1: Planar (1), heteroatom-doped (2) and twisted (3) derivatives of HBCs synthesised in the Draper team.](image)

Interestingly although large polycyclics incorporating up to 222 carbon atoms have been characterised, very few include an organometallic moiety \(^{(3)}\) and there are only three examples of a metal π-complex of 1 (one is illustrated in Figure 2). There is even less work on twisted aromatics (3) where the electronic platform is less delocalised and potentially more reactive.

![Figure 2: Molecular structure via single crystal X-ray diffraction of [(C\(\text{H}_{12}\))Rh(h\(\text{C}_6\)-1)][BA\(\text{F}_4\)]. Showing dimeric-stacking of molecules. H atoms and counter anion not shown](image)

Having prepared the organometallic counterparts of these systems it is possible to determine – how the HOMO-LUMO gap varies on coordination and influences electron transfer from metal centre to aromatic plane. The integration of this type of information is important for establishing its structure/property characteristics and opto-electronic applications where alignment and stacking are very important.

References:
Hydrothermal Injection Synthesis of Hydroxyapatite Nanomaterials

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Research Project Description:
As the major component of hard tissues, such as bones and teeth, hydroxyapatite (HA, Ca_{10}(PO_{4})_{6}(OH)_{2}) is a hugely important bioceramic, and synthetic HA has been widely investigated for a variety of biomedical applications including bone regeneration, tissue scaffolding, and drug delivery.\(^1\) Understanding the formation of HA and exerting synthetic control over particle size and shape is thus of great interest. HA formation may proceed through complex multistep pathways via amorphous calcium phosphate or octacalcium phosphate species, which may significantly affect the final morphology.\(^2\) Synthetic control relies on influencing the nucleation and growth behavior, typically by varying reaction parameters such as pH and supersaturation, or by the incorporation of surface modifying additives.\(^2\) Among the many synthetic approaches which have been investigated, hydrothermal processing, which uses superheated, pressurised water as a green reaction medium is among the most attractive.\(^5\)

In this project we will explore the use of a recently developed hydrothermal injection reactor which allows for precise control of nucleation and growth conditions (Figure 1) for the shape-controlled synthesis of hydroxyapatite nano- and micromaterials. The student will gain experience in reactor design, materials synthesis, and characterisation techniques including powder X-ray diffraction, infrared and Raman spectroscopy, and electron microscopy.

References
Mesoporous Metal Oxides from Nano-Building Blocks

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Research Project Description:
Mesoporous materials are high surface area solids which contain pores with diameters of 2-50 nm. These materials may be comprised of amorphous or poorly crystalline walls with ordered or disordered pore geometries. Mesoporous silicas, such as MCM-41 and SBA-15, are common examples of amorphous silica forming ordered mesoporous solids. Such mesoporous materials exhibit high surface areas, and consequently are much sought-after and widely used in catalysis and drug delivery applications.1-2

Typically, such mesoporous materials are prepared by the self-assembly of surfactants to generate micellar structures which act as templates for the deposition of the inorganic wall material by sol-gel precipitation. Subsequent calcination removes the surfactant template leaving the low-density, high surface area solid. Despite 30+ years of research in the area, obtaining mesoporous materials beyond silica remains a challenge. Even simple mesoporous binary metal oxides are difficult to prepare owing to higher hydrolysis rates of metal oxide precursors and poor mesopore stability due to crystallization induced collapse of the porous frameworks.3 More complex mesoporous doped oxides and ternary oxides remain highly elusive.

Here we aim to use well-defined pre-formed metal oxide nanocrystals as building blocks for the generation of high surface area mesoporous metal oxides. Simple sol-gel and/or solvothermal syntheses will be used to generate sub 5 nm metal oxide nanoparticles capped with organic ligands. These organic ligands may interact with the surfactants used in the generation of mesoporous templates allowing the self-assembly of these defined nano-building blocks into complex mesoporous structures, or their incorporation into templated silica hosts, as in shown in Figure 1.4

The student will gain experience in sol-gel and solvothermal synthesis of surface modified metal oxide nanoparticles and soft-templating by self-assembly systems. A range of techniques will be employed to characterise the obtained materials and their intermediates, including powder X-ray diffraction, electron microscopy, and spectroscopic methods.

References
New membranes for water purification

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Research Project Description:

Introduction
Water for both domestic and industrial use is becoming a scarce and expensive resource requiring careful control and protection. Membrane based separation systems dominate the European market for industrial process water treatment equipment. In particular, recently new nanotechnology-based solutions (nanofiltration) have emerged as potentially superior and cost-effective ways to remove sediments, charged particles, chemical effluents, bacteria and other pathogens in addition to the removal of toxins like arsenic or impurities like oil [1]. However, biofouling of membranes is a severe and common problem. The growth of biomass on the surface of membranes and adsorbents (biofouling) limits both the efficiency (volume treated per unit time) and lifetime of systems and necessitates periodical washing of the membrane equipment with aggressive chemicals. There is, therefore, a pressing need to develop antifouling systems that exhibit active durability and are eco-friendly.

Objectives
The main goal of this project is to develop new nanofiltration approaches and membranes for complex water purification. In this project, biofouling issues and other related problems will be addressed via development of a new generation of active membranes with potential anti-fouling properties which will be designed and engineered at low cost. The increasing safety of NMs is of particular importance and we will implement the necessary measures to prevent the occurrence of nanoparticles in treated water, using our membrane design in addition to filtering pre-existing particles from water. New membranes of varying compositions and porosity will be tested to determine the optimal water treatment conditions.

Expected outcomes
The successful realisation of this project will result in the development of new nanostructured adsorbents and membranes with enhanced bactericide and anti-biofouling activity, which will allow removal of various contaminants including bacteria, oils, grease, dyes, detergents, colloidal substances, toxins, pesticides, drugs and antibiotics from water. The special purity water will be particularly important for food industries in Ireland, for example for production of various drinks and dairy products. The exploitation of new membranes will give potential users more reliable, cost efficient treatment that generates high quality water, with a tailored mineral content.

References
New Luminescent Solar Cell Concentrators

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Research Project Description:

Introduction
Sunlight provides the largest of all carbon-neutral energy sources. The luminescent solar concentrators (LSCs) offer the opportunity to concentrate both diffuse and direct sunlight and have a number of important potential applications including: solar cells, integrated photovoltaics, smart windows, greenhouses, and glazing in buildings. LSC is in its simplest form is a slab waveguide, of usually rectangle dimensions as shown in Figure 1, designed to concentrate light incident on its top face to its edges [1, 2]. Normally LSCs involve the use of a photoluminescent dye-doped matrix, which firstly absorbs incident sunlight and reemits it in the form of fluorescence. These emitted photons radiate in all directions from the dye, with a certain portion of them being trapped by the LSC due to total internal reflection, which is dependent upon the refractive index of the matrix. Hence, due to the difference in surface area of LSC edges relative to its top surface, light is concentrated at the edges. Therefore, if a solar cell is then attached to the edges a large increase in the solar cell power is found to take place.

Objectives
The main aim of the project is to develop new luminescent solar concentrators formed from transparent polymers (e.g. polymethylmethacrylate, PMMA) and non-toxic semiconducting nanocrystals, quantum dots (QDs). In this project we plan to use non-toxic QD based luminophores, that maintain the preferable photophysical aspects mentioned, while avoiding the pitfalls. The research work will include following technical tasks: (i) QD preparation and characterisation; (ii) new LSC design and fabrication; (iii) LSC-solar cell tandem prototyping and testing.

Expected outcomes
The successful realisation of this project will result in the development of new LSCs, which will then be integrated to a range of commercially available solar cells. A selected LSCs and photovoltaic cells will be tested including, monocrystalline and polycrystalline Si-based cells.

References
Multimodal magnetic core-shell nanoparticles

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Research Project Description:

Introduction

Multimodal magnetic nanoparticles have been used for a broad range of applications including catalysis, cell labeling, drug delivery, hyperthermia treatment and biological imaging (e.g. see Figure below) [1, 2]. The focus of our research is the development of new magnetic nanostructures and their conjugates to be used as potential theranostic tools in cancer research. These structures possess the unique advantage of the large surface area and small size characteristic of nanoparticles, coupled with the magnetic modality required for biological imaging and drug delivery.

![Image of multimodal magnetic nanoparticles](image-url)

Objectives

The main goal of this work is to develop new multimodal magnetic nanocomposites for biomedical (e.g. MR and CT imaging and cancer therapy) applications. Magnetic oxide core-shell nanostructures will be synthesised using co-precipitation and other processing techniques. The characterization testing and evaluation of new materials will be performed by electron microscopy, FTIR, Raman spectroscopy and magnetization measurements. The nanomaterials will be functionalised with specific biomarkers and drugs and will be tested for potential in vitro and in vivo cancer diagnostic and therapy.

Expected outcomes

The successful realisation of this project should result in the development of new multimodal magnetic nanomaterials, which could serve as MRI and CT contrast agents and vectors for drug delivery in cancer therapy.

References

Mimicking Class Ib Dimanganese Ribonucleotide Reductases

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Research Project Description:
The research proposed herein will address the Chemistry of a family of enzymes that play a pivotal role in human health. You will perform a project in the area of Bioinorganic Chemistry. You will explore the natural Chemistry of a family of enzymes called Ribonucleotide Reductases (RNRs). RNRs employ dioxygen and manganese for the biosynthesis of deoxyribonucleotides, precursors to DNA.

You will attempt to gain an understanding of the mechanism and intermediates of the reactions these enzymes catalyse. This will help us to understand their biochemistry, and develop treatments where these metal-containing enzymes are performing adversely. You will develop synthetic small-molecule analogues of the active site of these enzymes. These small-molecule compounds will display the same physical properties as the enzymatic active site.

You will focus on a single aspect of the postulated reaction mechanism, that is the reaction of a derivative of dioxygen, called superoxide, with dimanganese (and other bimetallic) complexes. Superoxide interacts with the metal site in these enzymes producing a so-called metal-peroxide intermediate. You will synthesise metal-superoxide complexes and investigate their reactivity properties. In investigating these model compounds, we will probe the kinetics of these reactions, identify the products of reactions, and try to verify the postulated reaction mechanism for the RNRs.

The outcome of these investigations will be particularly exciting, because it will provide the first and the only experimental investigations into certain biochemistries of this large family of metalloproteins. You will utilise organic and inorganic synthetic methods in this project, learn how to perform reactions under exclusively anaerobic conditions, as well as gaining skills in a variety of spectroscopic techniques.

References:

High-Valent Metal-Halide Oxidants

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Research Project Description:
The oxidative functionalization of inert C–H bonds in hydrocarbons is an important transformation in biological systems as well as industrial catalysis. A large numbers of Fe- and Cu-containing metalloenzymes perform such hydrocarbon oxidations, forming hydroxylated, halogenated, or desaturated hydrocarbons. It has been proposed that such reactions involve hydrogen atom transfer (HAT) from an inert C–H bond to a high valent metal based oxidants such as metal-oxo (M=O) and M-OX (OX = OH, OR, O2C-R, ONO2). However, the HAT reactivity of the metal-bound halide in C–H/O-H activation has rarely been studied, although we postulate there will be a very high driving force for such oxidations.

The major objective of this project will be to prepare a series of metal-halide (Ni, Cu) complexes supported by stable and robust ligands. You will prepare high-valent derivatives of these complexes and subsequently investigate the reactivity of the corresponding high valent metal halide complexes towards hydrocarbons. It will also be a goal to explore the oxidative halogenation of hydrocarbons using such compounds. You will utilise organic and inorganic synthetic methods in this project, learn how to perform reactions under exclusively anaerobic conditions, as well as gaining skills in a variety of spectroscopic techniques.

References:
Functionalisation of 2D Nanomaterials for Catalysis

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Research Project Description:
Molybdenum disulfide (MoS$_2$) is a widely used catalyst for important industrial processes like hydodesulfurisation and hydrocracking of petroleums (it is used to remove sulfur containing molecules from fuels, limiting emission of SO$_2$ gas). Furthermore, MoS$_2$ is a highly reactive hydrogen evolution catalyst. We explore the reactivity properties of two-dimensional (2D, analogous to graphene) MoS$_2$ nanosheets for applications in hydodesulfurisation and hydrogen evolution catalysis. We expect exceptional enhancement in catalytic efficiency when moving from bulk MoS$_2$ to 2D MoS$_2$ nanosheets. We attribute this to the increase in S vacancy defects and Mo free sites present at the edges in the delaminated (2D) nanomaterials. These sites are known to facilitate adsorption of reactive molecules onto the catalyst surface, and therefore may enhance reaction rates.

This project will focus on the exploration of the reactivity properties of 2D MoS$_2$ (and functionalised derivatives thereof) in hydodesulfurisation and hydrogen evolution reactions. You will prepare 2D MoS$_2$ nanomaterials, characterise them using an array of spectroscopic probes (UV-vis, FT-IR, TGA, XRD, XPS, Raman). You will then optimise the reactivity properties of the 2D nanomaterials.

References:


Self-assembly in Large Molecular Weight Block Copolymers for Nanopatterning Applications

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Research Project Description:

The self-assembly of large molecular weight block copolymers into spatially oriented nanodomains has opened up a range of new possibilities in the manufacture of sub-wavelength optical nanostructures, such as Si nanopillars for anti-reflective coatings. In order to obtain such effects in the visible spectrum, the block copolymer domain sizes need to be greater than 100 nm. These have been synthesized thus far by our group using high molecular weight PS-b-P2VP block copolymer thin films on silicon substrates.

![AFM topography image of (PS-b-P2VP), (b) Si Nanopillars synthesized using PS-b-P2VP as a mask mimicking moth eye (c).](image)

This project will aim to expand on this work, examining the formation of domains using other molecular weights and families of block copolymers. Varying molecular weights of polystyrene-b-2-vinylpyridine (PS-b-P2VP) will be tested, along with high molecular weights of polystyrene-b-polyethylene oxide (PS-b-PEO). PS-b-PEO has shown strong potential for nanostructure fabrication, however the domain sizes thus far have remained below that required for optical applications in the visible spectrum. The phase separation of high molecular weight block copolymers is little understood, and will need to be optimized for these new polymer systems. This will involve the fine-tuning of each process outlined below in the synthesis route – including the polymer solution concentration, phase separation process, and ethanol swelling. In terms of characterization, the feature spacing, film coverage, diameters and structural characteristics for each block copolymer will be examined and compared.

If successful, nanostructures will be generated using metal infiltration these onto silicon and glass substrates, which will be etched to produce nanoscale features. It is hoped that this work will lead to the formation of a variety of morphology and feature sizes, each of which could be utilized for different nanostructure applications.

References:
Large Area Nano-porous graphene Membranes Derived from self-assembled Block Copolymer Lithography

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Research Project Description:

Highly selective and high-permeable membranes are the scope for the future separation technology to address the limitations of the current membrane technologies. An efficient membrane should compete in four main criteria: high selectivity, high permeability, mechanical integrity, and resistance to fouling. Two-dimensional (2D) materials are an ideal alternative for fabrication of ultrathin membrane which promises ultimate permeation. Among 2D materials, Graphene owing to chemical stability, and inherent impermeability offers a unique 2D membrane if perforated precisely. Despite the fact that many researches has been conducted so far on generating nanopores on graphene using various techniques, yet there is a lack of efficient and reliable method to produce graphene membrane in large scale.

The aim of this project is precisely perforate graphene oxide and graphene nanosieve using a unique block copolymer nanopatterning method with up to 108 pores/cm² of hexagonally ordered pores with uniform size and distance from less than 10 nm up to few 100 nm. Nanoporous graphene membranes derived from this method have tremendous promise to fulfil all four of those requirements due to their narrow pore size distributions (high selectivity), high porosity (high permeability), robustness and antifouling properties.

Two strategy will be employed to create nanopores on graphene using two different type of block copolymers (showed in schematic diagram) (PS)- block-poly(4-vinylpyridine) (PS-b-P4VP) (d) and polystyrene-block-poly(dimethylsiloxane) (PS-b-PDMS) (e). This method is based on periodic micro-phase separation of the two incompatible blocks at equilibrium conditions to lead the minimal free energy configurations. The nanostructures can then be used as masks for pattern transfer to graphene via Reactive Ion Etching (RIE) and oxygen plasma. This approach integrating large-area graphene film with block copolymer lithography is potentially advantageous in creating 2D atomically thin membranes with predefined pore size for efficient separation of specific molecules with desired size.

Figure 1. Schematic of fabrication technique

References


Lo, Ting-Ya, et al. "Silicon-containing block copolymers for lithographic applications." Progress in
Block-copolymer Templated Silicon Nanoporous Monolith Embedded with AuNPs: Application in Confined Space Photocatalysis

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Research Project Description:
Metal nanoparticles are well known for their ability to produce large, localized electric fields. It has been observed that for multiple particles confined in nanostructured spaces, the enhancement of this near-field due to the plasmonic coupling is greater than for dispersed, isolated nanoparticles [1,2]. When the separation between nanoparticles is sufficiently small, the conduction electrons near each nanoparticle surface become delocalized and are shared between adjacent nanoparticles resulting in an electric field enhancement [2]. The plasmonic nanostructures with a tunable light-matter interaction have potential applications in efficient light harvesting applications such as photocatalysis, artificial photosynthesis, photovoltaics, water purification, and imaging and microscopy techniques, e.g., medical diagnostics.

The objective of this project is to study the effect of confinement plasmonic photocatalysis.

Block-copolymer (BCP) soft-nanolithography is a versatile, robust, and cost-effective technique to nanostructure surfaces and produce a variety of surface morphologies such as nanopillars and nanocavities [3,4]. You will learn a new fabrication technique based on self-assembly of block-copolymers to produce nanostructured surfaces. During this research project we will employ poly(styrene)-block-poly(methyl methacrylate) (PS-b-PMMA) BCP (scheme 1) to define an etch mask for producing a nanoporous silicon substrate with gold nanoparticles embedded in it for photocatalytic applications. In the next step gold nanoparticles will be confined in nanopores. The advantages of this system are its high surface area, the ability to easily separate the photocatalytic monolith from the reaction system, and the close proximity of the metal nanostructures confined in the nanopores to couple plasmons efficiently. To investigate the activity of this platform, we will test different common pollutants such as dyes and their degradation under mild environmental conditions. We anticipate findings from this research will have potential applications in light harvesting energy materials and water purification.

References
Study of the effect of water concentration on nitrocellulose membrane formation

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Nitrocellulose membranes are used in a range of applications ranging from bioassay through to separation and purification. They are commonly prepared by a process of inverse phase separation where a solution of nitrocellulose (NC), acetone (solvent), water and other non-solvents is subject to a thermal or concentration change to cause polymer precipitation. The non-solvents act as pore formers to create the membrane structure. The pore size, pore volume and the appearance of the membrane is dependent on many parameters including water concentration. This project will seek to understand the relationship of membrane properties to water concentration by defining a phase diagram mapping morphology over a range of NC, solvent and non-solvent concentrations. We will extensively use light scattering to measure polymer aggregation and precipitation, microscopy to look at membrane morphology and quantify fundamental properties such as pore size, porosity and flow times.

Objectives:
- a) To prepare NC by inverse phase inversion that have mean pore size of 2 - 15 μm
- b) To define the NC phase diagram as function of solvent and non-solvent concentration at a 14 – 16% NC concentration
- c) To rationalise observations using solvent theories

Outcomes:
This work should contribute to publication of a journal paper. It should also help to define future manufacturing methods for NC production

References
1. M Ulbricht, Polymer, 47 (2006) 2217
Towards $H_2$ Economies: 4th Generation Metal-Organic Frameworks for Photo/Electro-Catalytic Device Fabrication

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Scientific objectives: The project addresses the question of how catalytically active Metal-Organic Frameworks (MOFs) or light-harvesting MOFs can be synthesised deposited or printed on electrodes to produce electro/photo-catalytic devices. The systems will be used to catalyse highly endergonic, energy-related chemical transformations (e.g. $H_2O$ oxidation, $CO_2$ reduction, $H_2$ formation). The performance of the devices incl. catalytic activity, stability and efficiency will be investigated.

Scientific background: MOFs are regarded as key compounds related to energy storage and conversion, as their unprecedented surface areas make them promising materials for gas storage and catalysis.\textsuperscript{1} We believe MOFs allow the replication of key features of natural enzymes thus demonstrating how size, shape, charge and functional group availability greatly influences the guest binding and performances in catalytic reactions.\textsuperscript{2,3} In view of sustainable energy-related applications, the research project is directed towards electro/photo-catalytic systems. Photosynthesis is the process by which plants, algae and some bacteria use light energy to split water and use the released electrons and protons for the reduction of $CO_2$ to produce sugars. The process stores energy in chemical bonds. Insights into molecular details of these conversions can guide us towards employing renewable energy sources to produce fuels in highly porous MOFs whereby the term ‘fuel’ in a broader sense can be thought of as a reduced molecule that can efficiently be oxidised to produce desired compounds or energy as required.

The project will involve on the following defined parts:

- **Synthesis of MOFs**: This task will involve the preparation, structural and physicochemical characterisation of MOFs using novel, catalytically active clusters and organic linkers. The applied methodologies are well established with the research group.
- **Deposition of MOFs on electrodes**: The heterogeneous MOF materials will be interfaced or electrochemically deposed a the electrode materials.
- **Characterisation of the electrodes**: Characterisation techniques will involve electron microscopy techniques, X-ray diffraction and spectroscopic methods (Raman spectroscopy & XPS).
- **Electro-catalytic reactivity studies**: The electrodes will be applied to catalyse highly endergonic, energy-related oxidation or reduction reactions (e.g. $H_2O$ oxidation, $H_2$ production or $CO_2$ reduction). The performances and the stabilities of the electrodes will be optimised.

Physical, Computational and Materials Chemistry
Functionalisation of Electroactive Small Organic Molecules for Diagnostic Model Systems

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Research Project Description:
Given the periodic emergence of new and old infections, and the pressing challenges from antimicrobial resistance and pandemic threats such as Ebola and Zika, modern, disease-relevant methodologies represent critical target for improving our knowledge of the dynamics of host-pathogen interactions in their natural environment. Although many traditional models provide valuable tools for studying the mechanism of action of drugs there is a pressing need to revisit cell culture assay systems, to develop new models, and innovative screening technologies that better recapitulate in vivo physiology. In this context, functional organic electroactive materials are showing significant advancement in the development of in vitro model systems as well as diagnostic and implantable devices. The capability of organic electronic materials, in fact, in conducting and processing both electronic and ionic (bio)signals, tightly coupled via electron-ion charge compensation [1-3], lays the ground for the development of multivalent tools with enhanced sensitivity. Moreover, organic electroactive molecules can be designed via synthesis [4] to possess desired physical and chemical properties, thus enabling the manufacture of bioelectronics devices and systems that exhibit desired flexibility, elasticity, and morphology, and with a surface chemistry, that promotes biocompatibility and stability over extended periods [5].

Objectives. - Realisation of an electroactive organic film, ad-hoc chemically functionalised with bio-moieties such as glycans and membrane proteins. We will explore different functionalization approaches (i.e. direct chemical functionalization, physisorption/inclusion and plasma modification) to establish which strategies ensures a better recapitulation of the bio-moieties natural environment.
- Extensive surface and bulk chemical characterization of the system realized in order to investigating bio-moieties orientation, crowding and clustering. In addition, will be carried out an investigation into the electronic properties of the functional organic system, in order to determine the sensitivity of the novel material developed in probing disease-related ionic and electronic processes.

Outcomes. The student will acquire skills in processing and functionalization of small organic electroactive molecules with biomolecules, exploring different chemical and physical approaches. In addition, the student will be trained in electronic probing and electronic microscopies for the characterization of the electroactive material realized. The student will learn about interfacing biomolecules with organic systems, specifically they will gain insights into ionic and electronic transfer processes,

Figure 1: Representation of the functional electroactive system based on bio-functionalised small organic molecules in investigating host-pathogens interaction processes.

References
2D TMD modified membranes for filtration Applications

Prof. Ramesh Babu (RB1)

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Research Project Description:
Membrane filtration is one of the versatile and rapidly growing technology for advanced separation and water treatment applications. Hence, it is always of special interest to improve surface/bulk membrane properties for achieving desired multi-functionalities. Recent trends on developing layer-stacked 2D nanomaterials-based membranes is exciting for its great mechanical and physico-chemical properties. Emerging 2D transition metal dichalcogenides, like liquid exfoliated MoS\textsubscript{2} is holding greater potential in terms of nano-structural stability and water filtration capability than that of graphene oxide (GO), which has been reported to pose limitations in terms of fabrication complexity and membrane integrity towards pressure-driven water filtration applications.

By taking advantage of MoS\textsubscript{2} having strong Van der Waals structure with stable/narrow inter-layer spacing and many other desired properties suitable for application in aqueous environments, it is proposed to develop and characterize scalable/tuneable exfoliated MoS\textsubscript{2} nanosheets based polymeric membranes using approaches related to surface cross-linking or electrospinning methods. The overall aim of the project is to address the challenges in achieving fabrication scalability of MoS\textsubscript{2} based membranes for filtration applications.

Figure (1) Surface morphology of electrospun nanofibrous membrane\textsuperscript{1}, (a-insert) exfoliated MoS\textsubscript{2} doped ZnO (2) Scheme representing water transport through laminated MoS\textsubscript{2} nanosheets fixed on membrane substrate\textsuperscript{2}

References:
Research Project Description:

Pressure-driven membrane nanofiltration (NF) is known for its ability to separate solutes based on size exclusion and electrostatic repulsions. Because of NF membrane pore size and their charge properties, NF is promising process to separate low molecular weight compounds like divalent ions, heavy metals, sugars and so on, thus finding application ranging from food, dairy, pharmaceutical, effluent treatment and water purification among many. Yet, major limitation of NF exists in terms of achieving selective ion removal and susceptibility to fouling, which requires attention. Cross-flow electro membrane nanofiltration (CFEMF) process have the potential to conjugate the electrical field as an additional driving force to enable the charged molecules to move towards the oppositely charge electrodes. The synergistic combination of NF along with electric potential further helps in maintaining high productivity with reduced fouling.

This project aims on examining the performance of both commercially available ion-exchange membrane and indigenously developed surface charged/conductive NF membranes while separating ionic solutes of economic and environmental significance. The combined effects of electrical field, diffusion and hydrodynamic forces for solute permeation during CFEMF will be evaluated based on feed and NF membrane characteristics.

**Figure** (1) Scheme illustrating selective permeation through ion exchange membrane\(^1\) (2) Cross flow electro-membrane filtration cell (3) Working mechanism of electro-driven membrane filtration\(^2\)

**References:**

The morphology and stability of nanocrystalline metal films at few nanometer thicknesses

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Research Project Description:

Metals are the most abundant elements and crucial in all aspects of everyday life: from structural and mechanical engineering to facilitating electricity transmission to forming the tiny wires that connect each and every electronic device. There is an enormous interest in producing metals with improved mechanical and electrical properties to reduce energy losses and increase for instance the battery life of hand-held devices. We are leading this effort by investigating the properties of nanocrystalline metal films that are used to form the metal connections between individual transistors on a chip. The wires are sub-10nm, they are fragile and their ability to conduct charge diminishes as their size is reduced. Nanocrystalline metals are comprised of 20-50nm sized grains separated by grain boundaries. We have recently understood how grain boundaries can be exploited to enhance the stability of these films and this project will involve observing the evolution of the film structure as the thickness of the film is reduced by chemical etching. Specifically, this will entail a series of experiments to control the film thickness and then the use of atomic force and scanning electron microscopy to image the evolving surface structure and the subsequent thermal stability of the film. The latter measurement will be formed by determining the temperature that causes the film of ball-up on the substrate. The student will work as part of a team and training and mentoring will be provided throughout.

Figure: (a) The shape of the so-called triple junction groove between two grains in a copper nanocrystalline film. (b) is a close-up atomic resolution image of the structure of the groove. Controlling the groove shape and the structure of the grain boundary is key to controlling the electrical and thermal stability of the film

References
[1] Xiaopu Zhang, Jian Han, John J. Plombon, Adrian P. Sutton, David J. Srolovitz, John J. Boland. “Nanocrystalline copper films are never flat” Science 357(6349), P. 397-400, 28 July 2017
The Degradation of Polymers in Water

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Research Project Description:

Globally, there is a significant dependence on plastic products in our everyday life, from kitchen appliances and smart technology devices to food packaging and storage. The high demand for plastic results in around 380 million tons being produced annually (1). Most plastics are non-biodegradable, but can break down into small fragments known as microplastics (MPs) due to chemical and physical processes such as hydrolysis, oxidation, radiation and mechanical actions such as friction, scratching and others (2, 3). MPs have become an increasing global concern (3) due to their potential risk to the environment and to human health (4-6).

Using Raman and atomic force microscopy (AFM) mapping, we have investigated the quantity and size distribution of the MPs released from many standard plastic products. We have found that typically millions of MPs and trillions of nano-plastic are released per litre of water in contact with the plastic. This project involves a study of the mechanism of plastic degradation in the presence of water. The student will be part of a larger team and will receive mentoring and training on a wide range of imaging technologies, experiment design and statistical methods to estimate particle numbers.

Characterization and quantification of polypropylene (PP) microplastics. (A) Optical microscopic image of particles released from BFBs under with 100x microscope objective. (B) The Raman mapping of the same region obtained by PP Raman bands of 2830-2870 cm⁻¹. The color scale bar indicates the intensity of the integrated spectral band in arbitrary units. (C) The AFM image of the same region to determine the morphology of released MPs. The color scale bar indicates the height of MPs. (D) 3D AFM topographic image.

Sustainable materials for new energy technologies

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Description:
The interest in low-cost nanomaterials for electrocatalysis, has increased exponentially over the last few years. This results from the convergence of economic and societal demands for a more sustainable management of energy resources, with recent discoveries in the area of carbon materials for electrode applications. Electrochemical energy technologies such as fuel cells, metal-air batteries and water splitting are expected to play a key role in future energy solutions, however these technologies rely on the use of precious and/or scarce elements, thus posing severe limitations to the scale of their deployment due to cost and sustainability concerns. Replacement of scarce materials or significant improvements on the activity of current catalysts will be therefore necessary to ensure a cost-effective expansion of electrochemical conversion technologies. Low cost carbon materials and oxides of earth-abundant elements are interesting candidates for replacing or enhancing electrocatalysis of critical reactions for the energy economy.

The objectives in this project are to investigate the synthesis and properties of low-cost nanomaterials in electrocatalysis of reactions that are important for electrochemical energy conversion, e.g. the oxygen reduction and evolution reactions. Synthesis methods for disordered oxides and carbon nanostructured materials will be used to tailor catalytic activity in electrocatalysis while fundamental studies with diagnostic redox probes will be used to complement the understanding of these nanomaterials.

Tasks: You will prepare carbon and/or oxide nanostructured materials using one or more methods among ultraspray continuous flow, hydrothermal synthesis and/or batch surface modification of commercial nanomaterials. Figure 1 shows examples of electroactive materials prepared in our group using these methods. You will study the structure and properties of these new materials using a combination of spectroscopic (e.g. XPS, infrared), physical (e.g. contact angle) and electrochemical techniques (e.g. voltammetry, hydrodynamic techniques).

Skills: You will acquire expertise in surface characterization techniques for determining e.g. surface composition/chemistry, surface free energy, and in methods for establishing catalytic performance with standard redox probes (LSV, EIS) and with energy-relevant species (e.g. O₂, H₂O₂).

References:
Responsive Photonic Crystal Structures

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Research Project Description:
This project will utilise cutting-edge fabrication technologies, combined with stimuli-responsive materials to fabricate photonic crystal sensors. Photonic crystals are periodic assemblies, based on natural or synthetic structures, which can control the propagation of light, and therefore the reflected wavelength of light. To date, the fabrication of optical sensors, based on photonic crystals has followed two distinct routes: via advances in 1) materials or 2) structure design.¹ The former has relied on the deposition of functionalised nanomaterials, via sedimentation, spin coating, or vertical deposition, to form nanostructured responsive films.² The latter has relied on top down fabrication such as e-beam lithography, nano-imprint lithography or etching. This project aims to combine advances in highly-specific stimuli-responsive materials³-⁵, with high-resolution 3D fabrication. In this context, structures will be fabricated from stimuli-responsive materials, using direct laser writing by 2-Photon Polymerisation⁶ (Figure 1).

This project will involve investigating the effect of incorporating stimuli-responsive structures in the photonic crystal structures (during or post fabrication) and characterisation of the obtained structures by UV/Vis, Raman and FT-IR spectroscopy.

![Figure 1. Photonic crystal sensor. (Left) Diagram depicting the working principle of the sensor. The sensor consists of stimuli-responsive 3D structure fabricated by direct laser writing. (Right) SEM and reflection microscopy images of the 3D structures fabricated by direct laser writing.](image)

References
Research Project Description:
Hydrogels are three-dimensional, hydrophilic polymer networks, capable of water uptake. By incorporating molecular switches in their structure, stimuli-responsive hydrogel actuators can be developed, that respond to a variety of stimuli, such as light (Fig. 1), electric or magnetic fields, or a change in the local environment. The aim of this research will be to investigate the feasibility of using responsive hydrogels as micro-machines, capable of doing mechanical work in response to chosen stimuli. Moreover, new functionalities such as sensing, and switchable uptake and release of molecular guests, will also be incorporated in the same hydrogel material, in order to create synthetic units with biomimetic features.

During this project the student will explore several bioinspired microstructures based on stimuli-responsive hydrogels. The development of new synthetic protocols for functional monomers based on molecular switches and polymer optimisation will prove integral to this investigation. A variety of polymerization approaches will be investigated to control the nature of the hydrogel and to best translate the molecular change to a macro response. The project will involve synthesis and characterisation of the molecular switches using a variety of spectroscopic techniques (NMR, FT-IR, UV-Vis and fluorescence spectroscopy), the optimization of the fabrication process and complete characterization of the hydrogel structures (optical microscopy, SEM).

Figure 1. A) Schematic illustration of a photo-actuated hydrogel micro-walker; B) Chemical structure of the polymer used for the fabrication of the photo-actuated hydrogel micro-walker; C) SEM image showing the high porosity of the hydrogel material.

References
High-Throughput Modelling of Surface Coverages and Electronic Structure of 2D-Materials for (Electro)Catalysis

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Research Project Description

Two-dimensional carbides or MXenes\(^1\) are known to be readily functionalized with a variety of adsorbates such as O, OH, F, and H. These functional groups have been proven to confer a superior thermodynamic stability, which can be attributed to the similar electronic structure that functionalized MXenes adopt compared to their bulk counterparts. Functionalized MXenes are typically obtained by etching of a MAX phase (Figure 1A) with the general formula \(M_{n+1}AX_n\), where \(n\) ranges from 1 to 4, \(M\) denotes an early transition metal (e.g. Ti, Zr, Hf, V, Mo), \(A\) stands for an element from groups 13–16 (e.g. Al, Ga, In, TI, Si, Ge, Te), and \(X\) for carbon or nitrogen. Because of the high tunability and electronic properties, MXenes have been employed in a myriad of applications such as supercapacitors,\(^2\) wireless communications,\(^3\) as well as in a number of electrochemical reactions, including the oxygen evolution reaction,\(^4\) and hydrogen evolution reaction.\(^5\) These applications are often governed by the surface termination of MXenes, which depends on the reaction conditions.

This project aims to leverage state-of-the-art computational methods to conduct a high-throughput investigation of the surface coverages (Figure 1B) and electronic structure of experimentally reported MXenes. These new theoretical insights are expected to identify promising MXenes as (electro)catalysts for relevant industrial applications. By the end of this project students should demonstrate a deep knowledge of surface catalysis, electronic structure of 2D materials, and density functional theory methods.

![Diagram](image)

**Figure 1.** (a) Side view representation of a \(M_{3}AX_2\) phase along with its resulting MXene, \(M_3AX_2\). (b) Predicted surface coverages for \(Mo_3C_2\) at different applied bias.

References

Monitoring chemical transformations on plasmonic nanoparticles by Raman spectroscopy

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Metal nanoparticles can act as nanoscale antennas allowing them to funnel energy carried by light into nanoscale volumes on their surfaces. This funneling of light into nanoscale volumes can result in enhanced light-matter interactions in these regions. Consequently, these particles are of great interest for use in a new generation of photocatalysts and optoelectronic devices.\(^1\)

In this project, arrays of metal nanostructures fabricated by electron-beam lithography will be used to enhance photocatalytic processes. We have previously shown that metal nanoantennas illuminated at their resonant wavelength can emit electrons.\(^2\) Moreover, in recent work, we have shown that they can cause siloxanes such as HSQ to cross-link in specific regions on their surface that are determined by the antenna material and geometry, as shown in figure 1. In this work, Raman spectroscopy will be used to monitor chemical transformations on individual plasmonic nanostructures while illuminated at their resonant wavelength by a visible or near-infrared laser. This work will support the development of new catalyst materials and help improve our understanding of energy conversion processes in these systems.

During the project the student will have the opportunity to further develop their understanding of spectroscopic processes as well as surface science and catalysis. They will also learn about electron microscopy and nanofabrication by working with a postgraduate student and regularly discussing results with Dr. Hobbs.

Figure 1. (a,b) Scanning electron microscope (SEM) images of Au nanorods and nanotriangle antennas fabricated by electron-beam lithography. (c) SEM image of localized region of cross-linked HSQ at the centre of a Au nanorod after illumination with a laser that is spectrally matched to the surface plasmon resonance.

Synthesis of heterostructured plasmonic nanoparticles

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When metal nanoparticles are illuminated at certain characteristic frequencies, collective oscillations of conduction electrons called surface plasmons are excited resulting in amplification of electromagnetic fields on their surface. The amplified fields can drive localized chemistry at these surfaces, including for example, the dissociation of precursor compounds. The dissociation of precursor compounds on the surface of these particles will enable the synthesis of heterostructured plasmonic nanoparticles suited to applications in photocatalysis as well as providing new routes to nanostructure synthesis.1,2

In this project, nanoparticle arrays fabricated by electron-beam lithography3 will be used to drive dissociation of precursor compounds in solution phase. The student will characterize the optical properties of the nanoparticle arrays and perform experiments to dissociate precursor compounds on their surfaces. They will work with other group members to characterize the synthesized material by electron microscopy and spectroscopy. In this project, the student will investigate the use of different semiconductor precursor compounds for the synthesis of germanium, zinc oxide or titanium dioxide nanostructures suited to applications in photodetection and photocatalysis respectively.

Figure 1. Schematic of a Au-TiO$_2$ heterostructured nanoparticle operating as a catalyst for hydrogen evolution.1 In this work, plasmon-enhanced fields will be used to drive precursor decomposition in the desired locations to produce heterostructures with morphologies suited to catalyst and photodetector applications.

Bonding and Repulsion in Hydrogen Donor-Acceptor Pattern Recognition

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Research Project Description:
The accepted role of hydrogen-bonding in nucleotide recognition has been questioned by Kool et al. [1] who have suggested that complementary shapes, mimicking nucleotides, may alone be sufficient for discrimination (Fig. 1). Seddon and Evans however have questioned this view [2]. It is not necessarily a binary choice; the role of hydrogen donor-acceptor patterns in nucleotide recognition may be regarded as twofold, serving to bind associating complementary pairs, while simultaneously opposing non-complementary associations [3].

![Figure 1. Difluorotoluene (F), a Nonpolar Isotere for Thymine (T) [2].](image)

The evolutionary theoretician Eörs Szathmáry has developed a model for assessing the biological fitness of alternative alphabets with a view to explaining the particular genetic alphabet employed by nature [4]. While the results were interesting, the interactions energies he employed were very approximate. In this project Szathmáry’s model will be revisited, adapted where necessary, and using improved estimates of interaction energies. The project will involve Quantum Chemical calculations and a small amount of programming (though Excel may suffice).

The objective of the project will be to gain further quantitative insight into the relative importance of the repulsive and attractive components in nucleotide recognition, and thereby better understand the factors underlying the particular composition of the genetic alphabet (A, T, C and G) and as well as possible alternatives. The project should inform us on the robustness of Szathmáry’s model and his conclusions.

References
Tautomeric Instability and the Composition of the Nucleotide Alphabet

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Research Project Description:
Piccirilli et al [1] have demonstrated the chemical feasibility of incorporating novel base pairs into the genetic alphabet (Fig 1). The question therefore arises as to why nucleic acid sequences are assembled from the four bases G, C, A and U as opposed to an alternative or larger alphabet.

Some potential members of the genetic alphabet are rendered non-viable by reason of tautomeric instability. For example, the donor/acceptor pattern in iG is unstable, in contrast to that of G. The project will employ a variety of *ab initio* and semi-empirical quantum–chemical approaches to explore the underlying basis of the instability and will attempt to identify stable alternatives to A, T, C and G.

**Figure 1.** Potentially viable nucleotides divided by parity (a) the even-parity subset and (b) the odd-parity subset.

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[http://dx.doi.org/10.1038/343033a0](http://dx.doi.org/10.1038/343033a0)
Lego at Atomic Thicknesses: Characterization of Two-Dimensional Materials & Heterojunctions

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Consisting of layers of atoms less than a nanometre thick, two-dimensional (2D) materials, such as transition metal dichalcogenides (TMDs), have a huge range of interesting chemical, physical and electrical properties.\(^1\) However, by themselves materials typically have limited functionality - our world relies on combinations of materials and the interactions between them. It is logical that the focus of research on 2D materials has turned towards combining them with a view to tailored functionality and use in real-world applications\(^2\). Manual transfer of atomically-thin flakes of one 2D material on top of another offers a simple means to create heterojunctions on a laboratory scale\(^3\). This project will expand upon ongoing work in fabricating heterojunctions through mechanical exfoliation, surface enabled exfoliation and stamp transfer\(^3-^5\). A number of TMD and metal mono-chalcogenide combinations will be considered. To understand the nature of the heterojunctions they will be locally characterized by Raman spectroscopy and atomic force microscopy (AFM). In particular, advanced AFM modes such as conducting AFM (c-AFM) and Kelvin probe force microscopy (KPFM) will be used to investigate the changes in the materials brought about by stacking. There is also scope to further modify the structures through thermal sulfurization to produce Janus-like structures\(^6\).

References

Resistive Switching in Thin Films of 2D Transition Metal Dichalcogenides

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Non-volatile memory based on resistive switching is an intriguing research topic that has great potential for future use in the semiconductor industry. The resistance of such components depends on the history of the current that has passed through them, i.e. they retain memory of this.

Initial reports on resistive switching focused on thin films of metal oxides\textsuperscript{[1]}. In this case, the non-volatile resistive switching was attributed to ionic diffusion and the formation of conductive filaments. Recent reports have shown that 2D materials, such as transition metal dichalcogenides (TMDs), offer superior resistive switching performance\textsuperscript{[2,3]}. Such TMD-based devices typically involve a 2D layer, as thin as < 1 nm, sandwiched between metal contacts.

The ASIN group has considerable experience in the synthesis of TMDs by chemical vapour deposition (CVD) and related techniques\textsuperscript{[4]}. Initial reports indicate that films synthesized in this way may be suitable for resistive-switching applications\textsuperscript{[5]}. Within this project, the resistive switching performance of 2D materials grown in the ASIN lab will be assessed. The project will involve (1) vapour-phase growth of 2D TMD layers, (2) spectroscopic and microscopic characterization, (3) fabrication of electrical devices through maskless photolithography and (4) electrical characterization of these devices.

References
\textsuperscript{[2]} R. Ge, et al., Nano Letters, 18(1), 434-441, (2018)
\textsuperscript{[3]} S. Bhattacharjee, et al., ACS Applied Materials and Interfaces, 12(5), 6022-6029, (2020)
\textsuperscript{[4]} C. Yim, et al., ACS Nano, 10(10), 9550-9558, (2016)
Investigation of the Thermoelectric Properties of 2D Transition Metal Dichalcogenides

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Recent theoretical studies show Group VI transition metal dichalcogenides (TMDs) may make for promising thermoelectric (TE) materials for medium temperature (600-900 K) power generation.[1] However, very few experimental TE studies exist for this set of materials in the literature. This project seeks to fabricate TMD films (MX$_2$ where M=Mo or W and X=S or Se) using the thermally assisted conversion (TAC) process,[2, 3] which will then be tested thermoelectrically using charge coupled device thermoreflectance (CCD-TR).[4] CCD-TR can be used to measure temperature changes due to changes in the reflectivity of the sample and can separate the contributions from Joule heating and Peltier heating/cooling. This allows extraction of the thermoelectric power or Seebeck co-efficient in units of V/K. With additional measurement of the electrical conductivity, one can calculate the power factor for these materials which serves as a measure of their usefulness as thermoelectric materials at a given value of thermal conductivity.

Commercial thermoelectric materials based on Bi$_2$Te$_3$ are most often employed as a solid solution, alloyed with isoelectronic Sb$_2$Te$_3$ and Bi$_2$Se$_3$ in the interests of attenuating phonons without appreciably impeding charge carrier transport to decrease the thermal conductivity. With this in mind, once the pure TAC TMD materials have been characterised and compared thermoelectrically, if time permits the two best power-factor materials may be paired and fabricated as a solid solution alloy.

References

Development of ultra-thin energy storage devices based on two-dimensional nanomaterials

Prof. Valeria Nicolosi (VN1)
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Research Project Description:
Energy storage will be more important in the future than at any time in history. Climate change and the decreasing availability of fossil fuels require society to move towards sustainable and renewable resources. As a result, we are observing an increase in renewable energy production from sun and wind, as well as the development of electric vehicles or hybrid electric vehicles with low CO₂ emissions. Because the sun does not shine during the night, wind does not blow on demand and we all expect to drive our car with at least a few hours of autonomy, energy storage systems are starting to play a larger part in our lives. Supercapacitors store energy electrochemically, using reversible adsorption of charges of an electrolyte onto two porous electrodes and the formation of the so-called electric double layer at an electrode/electrolyte interface (see figure below)¹. We plan to use thin layers of conductive two-dimensional nanomaterials²-⁴ and unexploited ultrasonic deposition technologies to produce more efficient, ultra-thin, flexible supercapacitors. The work will involve processing on large scale equipment, followed by detailed microscopical characterization.

Figure: Schematic of (a) a parallel-plate electrostatic capacitor; (b) an electrochemical supercapacitor.

References
4. V. Nicolosi et al., 340, 6139, 1420 (2013)
Doping Cu$_2$O – towards low cost photovoltaic cells.

Prof. Graeme Watson (GWW1)
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Research Project Description:
The sun offers an immense amount of free and clean power, which we have not yet begun to seriously exploit. Metal oxides are ideal candidates owing to their combination of low cost and high stability in aqueous solutions. Unfortunately the optical band-gaps of many metal oxides generally lie outside the visible range (> 3 eV) making them bad for solar applications. Despite immense effort, attempts to reduce the band-gaps of active oxides such as TiO$_2$ through dyes, doping or co-doping have not succeeded in providing a viable material.

Cu$_2$O was the first material for which a patent was granted for a photovoltaic material but despite its historical importance, Cu$_2$O never gained great interest. With a band gap of 2.1 eV the maximum efficiency predicted from the Shockley-Queisser limit [1] is around 20% with the current interest stemming from its natural p-type conducting properties [2] and potential for very low cost photovoltaic devices [3]. To generate the most efficient device, a homojunction cell [figure 1] in which both n-type and p-type Cu$_2$O are present would need to be fabricated, [3] although currently no viable way of creating (through doping) n-type Cu$_2$O has been found [4].

In this project we will use density functional theory to examine the defect chemistry of Cu$_2$O to determine (i) if improved p-type properties can be generated (e.g. by N doping) and (ii) if simple doping can generate n-type Cu$_2$O (e.g. by Cl doping). In addition we will look at the native defects (Cu and O vacancies, Cu and O interstitials) to determine if these defects can form in opposition to the doped defects.

References

The impact of grain boundaries on the ionic conductivity of doped CeO$_2$

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Research Project Description:

The grain boundaries within multi-crystalline materials give rise to structural discontinuities which result in specific GB structures, potential non-stoichiometry and the segregation of point defects, all of which can significantly alter the macroscopic properties [1]. As a consequence, grain boundaries and interfaces can control the properties of materials and hence they are vital to understanding and optimising their performance. Despite this, there is little understanding of the structure and even less on the effects of these interfaces on materials properties due to the inherent complexity of the issues and limited experimental techniques.

We have recently developed a method of predicting the structure of tilt grain boundaries using sophisticated polarizable forcefields and applied this to CeO$_2$ [2] and demonstrated the segregation of oxide ion vacancies to the interface resulting in enhance 2D diffusion (figure 1).

This project seeks to determine the impact of dopant segregation to the boundary on the ionic conductivity. Such data is important in understanding the impact of material processing in multi-crystalline materials for the electrolyte of solid oxide fuel cells.

References