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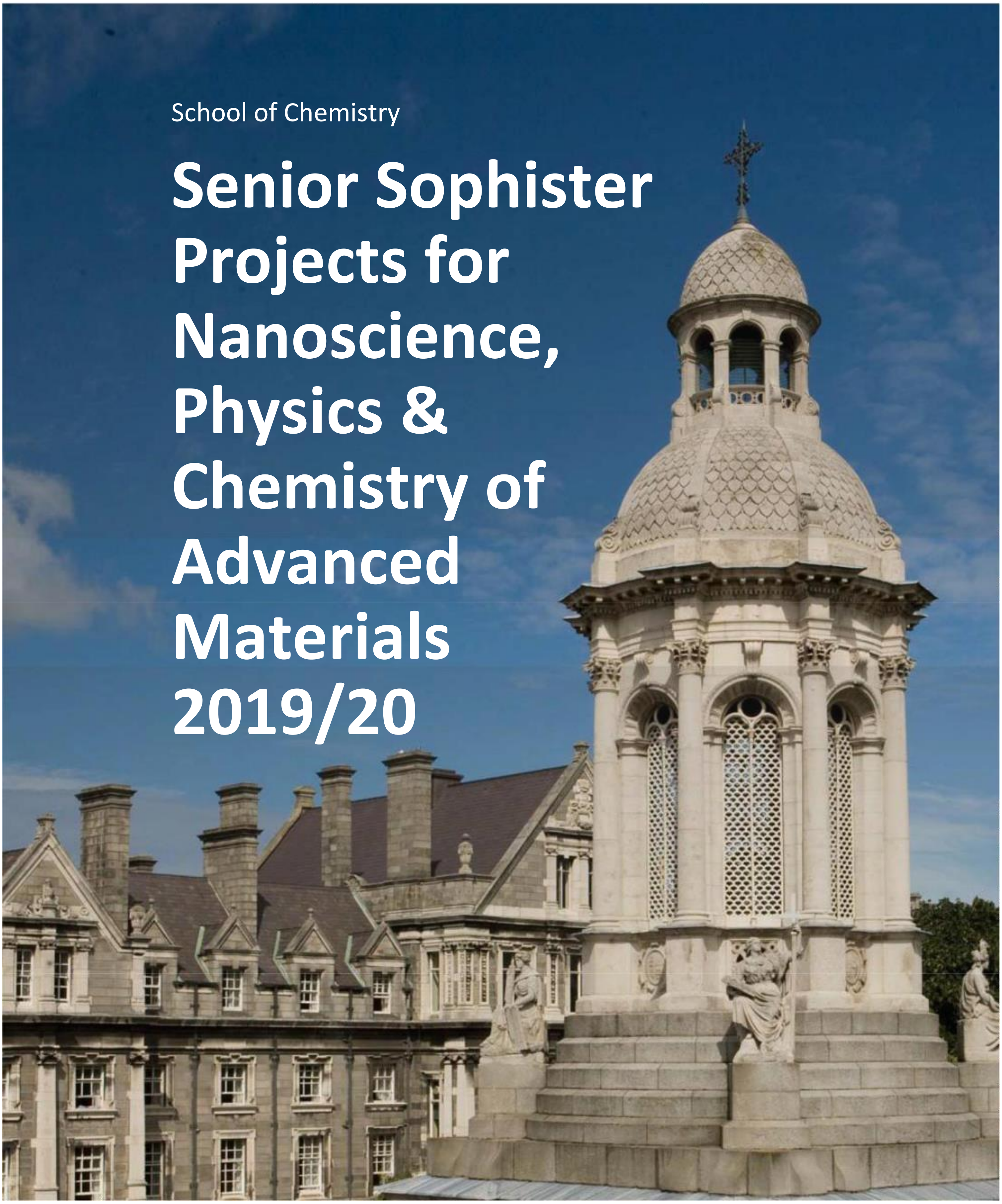

School of Chemistry

Senior Sophister Projects for Nanoscience, Physics & Chemistry of Advanced Materials 2019/20

School of Chemistry Senior Sophister Research Projects 2019/20

Contents

Inorganic and Synthetic Materials Chemistry

Compound Interest: Heavy Metal Complexes as Photosensitisers

Prof. Sylvia Draper (SMD1)
SNIAMS 2.5, ext 2026 smdraper@tcd.ie

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 sensitiser (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.

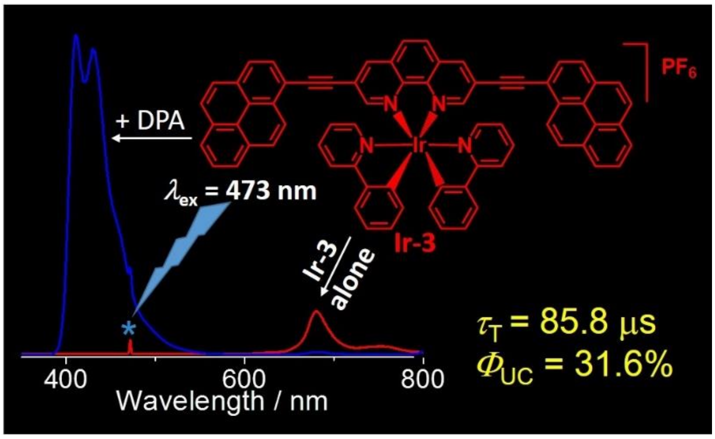

Figure 1: Emission spectra showing the sensitizer emission alone (red) and upconverted emission from DPA (blue) in a donor acceptor mixture (*exciting at 473 nm)

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.[2,3] 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.

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When it Glows: Hybrid Coordination Complexes with Photoluminescent Functionalities

Prof. Sylvia Draper (SMD2)

SNIAMS 2.5, ext 2026 smdraper@tcd.ie

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 polyphenylenes.[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 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.

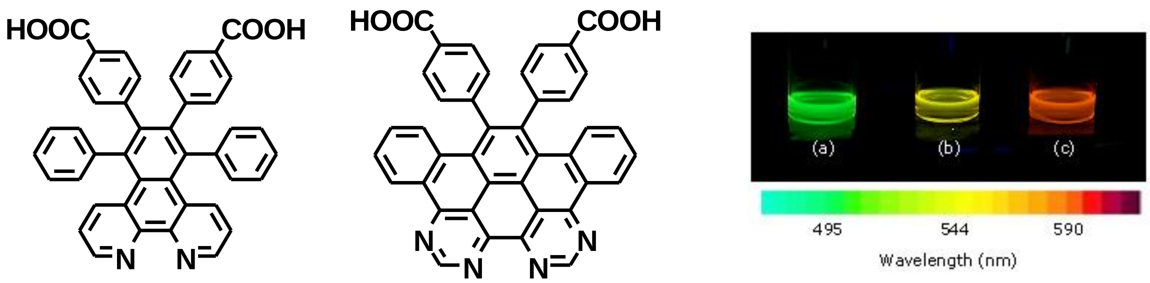

Figure 1 Proposed Ligands for generation of metal-based photoluminescent polymers

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

Prof. Sylvia Draper (SMD3)
SNIAMS 2.5, ext 2026 smdraper@tcd.ie

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.

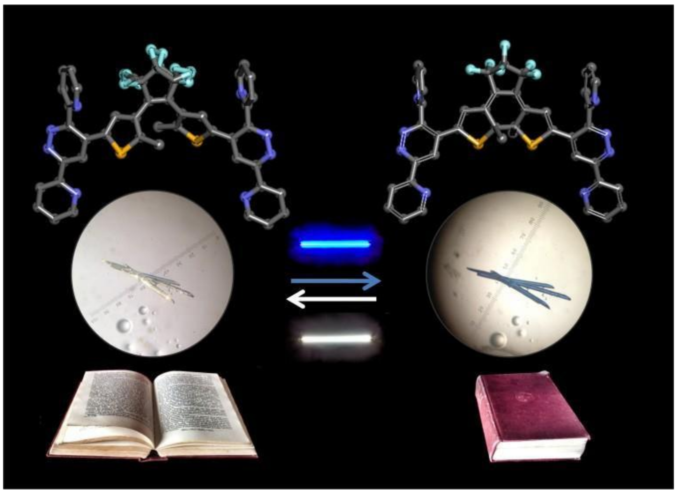

Figure 1: The Open (colourless) and Closed (blue) of crystals of a novel molecular switch

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

Prof. Sylvia Draper (SMD4)
SNIAMS 2.5, ext 2026 smdraper@tcd.ie

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$_3$))[1] giving little or no control of the position or % of the N-atom dopants (Figure 1 (a)).[2]

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[3,4] 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.

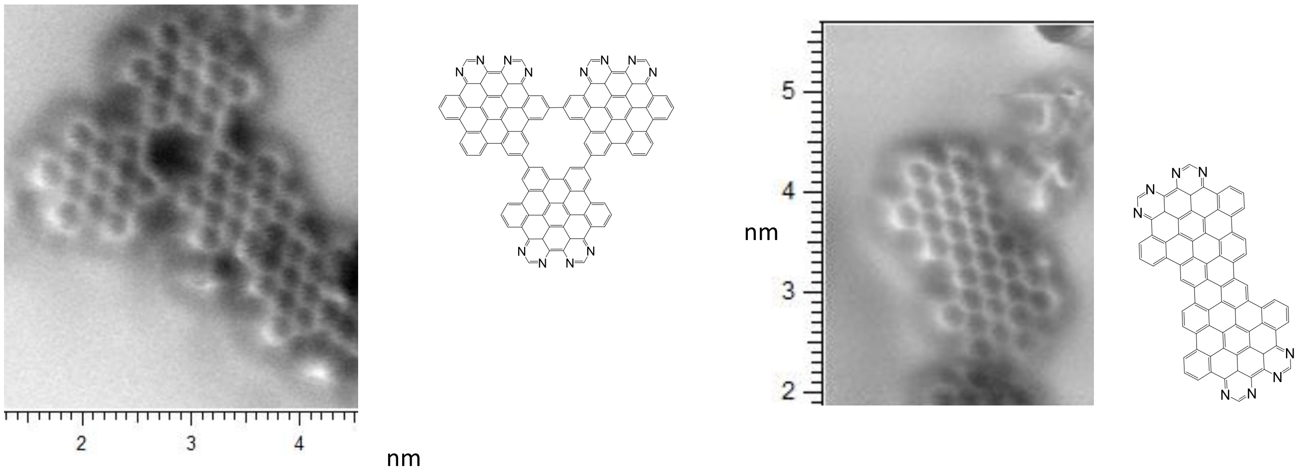

Figure 1 (a) Generation of N-doped graphene dimers via the thermal evaporation of precursors on Au (III) – Collaborator Prof. S. Decurtins

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Organometallic Polyaromatic Hydrocarbons

Prof. Sylvia Draper (SMD5)
SNIAMS 2.5, ext 2026 smdraper@tcd.ie /headchem@tcd.ie

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**)[1,2] 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.

1 2 3

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

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.

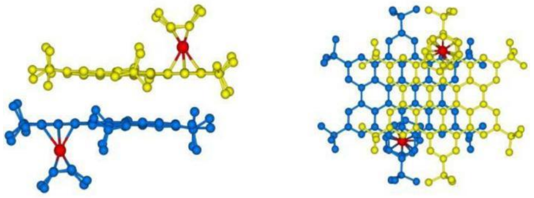

Figure 2: Molecular structure via single crystal X-ray diffraction of $[(C_8H_{12})Rh(h^6\text{-}1]][BAr^F{}_4]$. Showing dimeric-stacking of molecules. H atoms and counter anion not shown

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.

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Dispersible organic-inorganic hybrid nanomaterials

Prof. Peter Dunne (PWD1)

SNIAM 2.06; p.w.dunne@tcd.ie

Research Project Description:

Inorganic ceramic materials, such as metal oxides, find use in pigments,[1] catalysis, gas-sensing, and energy generation and storage. Typically, however, such ceramics are highly intractable and specialized techniques are required to produce the materials in the desired form; vapour deposition for coatings and thin-films, mechanochemical grinding for paints, *etc*. Nanocrystalline ceramics frequently present improved performance in many key applications, and importantly there is significant scope for surface modification of nanocrystals with organic capping ligands, conferring solubility to these otherwise intractable materials,[2, 3] as shown below in the case of tin oxide. Such hybrid organic-inorganic nanomaterials can be readily manipulated for the generation of dispersions, composites or coatings by simple wet-chemical methods.[4]

The synthesis of highly dispersible ligand stabilised metal oxide nanocrystals by a variety of wet-chemical methods, particularly hydrothermal and solvothermal routes will be investigated. The obtained materials will be characterized by a suite of techniques including powder X-ray diffraction, infrared spectroscopy and thermogravimetric analysis.

It is anticipated that this project will generate solution processable hybrid nanocrystals with potential applications across a range of industrial and technological sectors.[5]

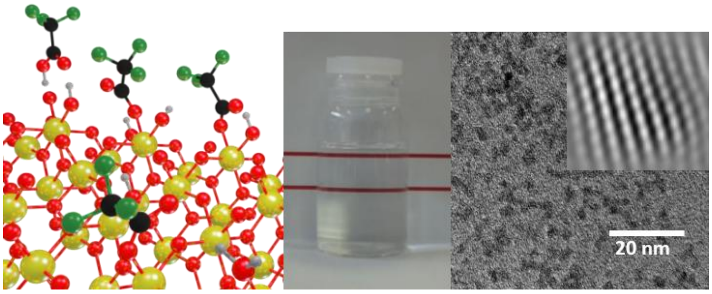

Figure 1: Highly soluble surface modified tin oxide nanocrystals.

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Hydrothermal injection for the phase and shape controlled synthesis of inorganic nanomaterials

Prof. Peter Dunne (PWD2)
SNIAM 2.06; p.w.dunne@tcd.ie

Research Project Description:

The properties of inorganic nanomaterials are highly dependent on their crystalline phase and shape.[1] Synthetic methods to control these properties are thus highly important. The well-established hot-injection process is among the most widely used synthetic methods for the size, phase and shape-controlled synthesis of inorganic nanomaterials, however a major drawback of this process is the requirement for environmentally costly high boiling point organic solvents and often toxic organometallic precursors.

Here we will use a newly developed hydrothermal injection process to produce inorganic nanomaterials using only water as a solvent. This project will target the phase and shape-controlled synthesis of materials which exhibit sphalerite-wurtzite polymorphism, such as zinc oxide and cadmium sulfide, as shown below. The crystalline phase of the initially formed nuclei, controlled by varying reaction temperature, is key to determining the morphology of the nanostructures produced.[2, 3]

It is expected that this project will help develop the hydrothermal injection technique and map the synthetic landscape around the hydrothermal production of polymorphic materials. The student will gain experience in materials synthesis and characterisation techniques, such as powder X-ray diffraction and electron microscopy.

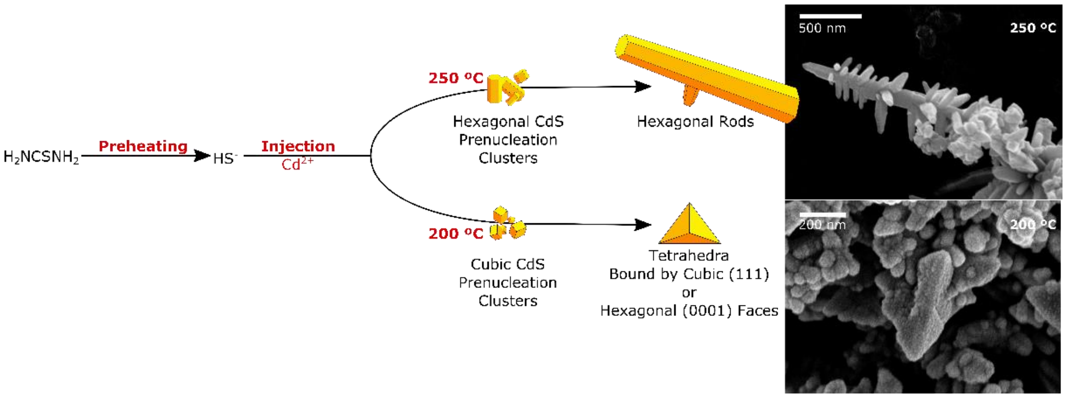

Figure 1: Cadmium sulfide nanostructures produced by hydrothermal injection at 200 °C (bottom) and 250 °C (top).

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Growth of hollow and plant-like microstructures from colloidal seeds

Prof. Peter Dunne (PWD3)

SNIAM 2.06; p.w.dunne@tcd.ie

Research Project Description:

Complex inorganic structures can exhibit very lifelike morphologies, as in the case of chemical gardens, which have been widely studied since the 1600s. There has been a recent resurgence in interest in such biomorphic structures as they may shed light on the processes of self-assembly employed by living organisms, and have been implicated in the origins of life.[1-3] Understanding and controlling the process which govern such biomimetic growth is thus of fundamental scientific interest and may lead to significant developments in applied areas of catalysis, sensing and microfluidics.

We have recently shown that easily prepared colloidal sulfur can act as "seeds" for the growth of complex life-like copper sulfide microstructures, as shown in Figure 1. These structures are formed by the initial generation of a semi-permeable copper sulfide shell. Subsequent infiltration of copper into the sulfur core leads to rupture of the hollow shell and growth of copper sulfide tendrils from within, giving morphologies which are highly reminiscent of germinating seeds and pollen. Here we will further refine these processes to achieve greater control over the obtained biomorphic structures and expand the synthetic protocols to allow the formation of a wider variety of metal sulfide microstructures.

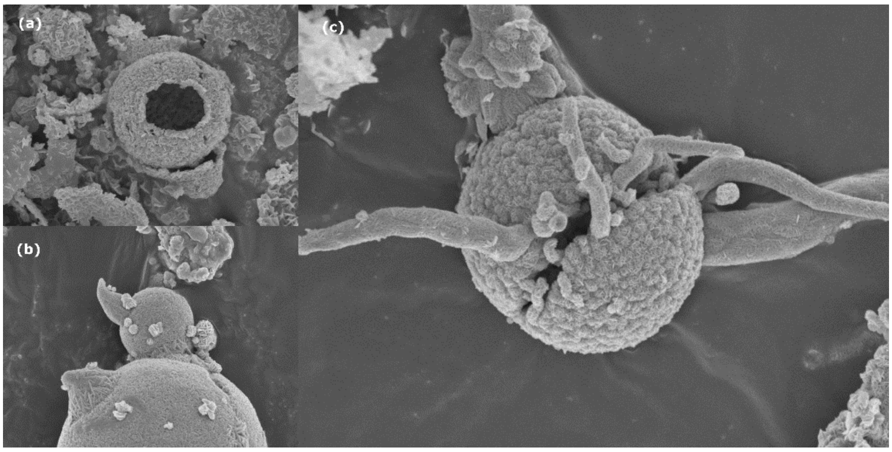

Figure 1: (a) Hollow microsphere, (b) budding pod, and (c) germinating pollen-like copper sulfide microstructures grown from colloidal sulfur seeds.

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Chiral nanoparticles for biological applications

Prof. Y.K. Gun'ko (YG1)
SNIAMS (room 2.02) igounko@tcd.ie

Research Project Description:

Introduction

Chirality is one of the key factors in molecular recognition, which has many uses in chemistry and biological systems. The development of chiral nanoparticles would present a great interest not only for nanotechnology, but also for many other fields of science including chemistry, biochemistry, pharmacology and medicine. In addition, the understanding of the fundamental concepts relevant to chirality in nanosystems is very important for the advance of nanoscience and nanotechnology in general. The use of stereospecific chiral stabilising molecules has also opened another avenue of interest in the area of quantum dot (QD) research [1-3]. This project is to explore new chiral light emitting nanomaterials and their potential biological applications.

Objectives

The main aim of this project is to develop new Cd-free chiral QDs (ZnO and ZnS-based) for chiral luminescent biological sensing. The initial goal in this project is to develop the synthesis of new chiral Cd-free QDs, using various chiral thiol stabilisers and to investigate their structure and optical properties. We plan to prepare a series of new chiral ZnO, ZnS and ZnSe based QDs using commercially available enantiomeric thiols (penicillamine, cysteine, glutathione) as stabilising ligands. New QD samples will be studied using various instrumental techniques. Correlations between the chiral and luminescent properties of these QDs and the nature of induced chiral defects will be investigated in detail.

Expected outcomes

Overall we anticipate that the successful realisation of this project should result in the development of new nanomaterials with a range of potential applications in biology and medicine.

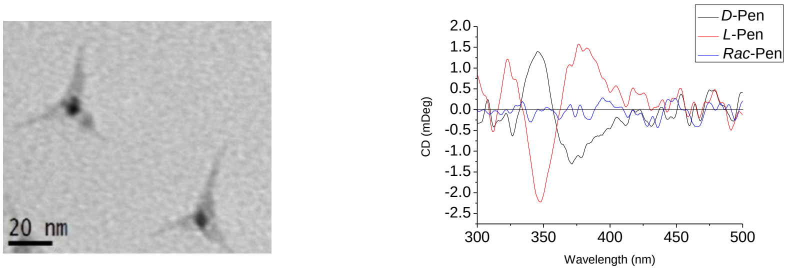

Figure: **A**: TEM images of chiral nanotetrapods, **B**: CD spectra of penicillamine stabilised CdS tetrapods [1].

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Magnetic and plasmonic nanoparticles for biomedical applications

Prof. Y.K. Gun'ko (YG2)
SNIAMS (second floor) igounko@tcd.ie

Research Project Description:

Introduction

Magnetic and plasmonic nanoparticles have been used for a broad range of biomedical applications including cell labeling, drug delivery, hyperthermia treatment and biological imaging (see Figure below) [1-3]. The focus of our research is the development of new "two in one" magnetic-plasmonic nanostructures and their conjugates to be used as 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 increased length required for sensing and drug delivery.

Objectives

The main goal of this work is to develop new multimodal magnetic-plasmonic nanocomposites for biomedical (e.g. MR and CT imaging and cancer therapy) applications. Magnetic oxide/ gold or silver and magnetic alloy-based nanostructures will be synthesised using hot injection 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 *in vitro* and *in vivo* cancer diagnostic and therapy.

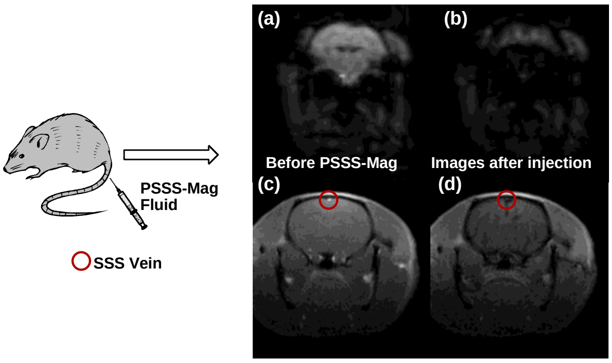

Figure: Echo planar image (EPI) of mouse brain (a) before and (b) as magnetite-based magnetic fluid passes through; Fast Low Angle Shot (FLASH) image of mouse brain (c) before and (d) as our new MRI fluid passes through.

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.

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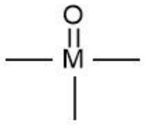
Synthesis and characterization of trigonal planar complexes with ANAM ligands

Prof. Aidan McDonald (AMcD1)
aidan.mcdonald@tcd.ie

Hydrocarbons-based feedstocks are still, despite the struggle for focusing on alternative energy sources, the most widely used source for more complex chemicals and energy production. C-C and C-H bonds are normally strong and consequently inert to functionalization, which thus requires harsh conditions leading to environmentally unfriendly and non-cost-effective processes [1]. A lot of these processes are also unselective, giving multiple products and undesired by-products - like the well-known greenhouse gas carbon dioxide. Therefore, the search for alternative, milder and more selective hydrocarbons functionalization methods is an utmost important and current challenge. The synthesis of biomimetic complexes inspired by active oxidant species involved in enzymatic catalytic cycles, notably metal-oxo intermediates, is one important route of investigation to overcome this limit.[2] Late transition metal-oxo complexes (groups 9, 10, 11) are postulated to be potentially stronger oxidants than early-transition ones, but they have so far been elusive due to electronic structural requirements.[3] One possible strategy to override this "Oxo Wall"[3] is to synthesize low-coordinate precursors in square planar, tetrahedral or trigonal planar geometries (figures 1, 2, 3).



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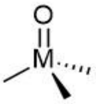

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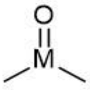

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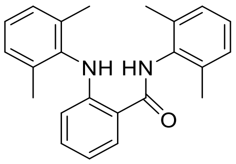
Aryl-substituted anthranilamides (ANAM = ANthranilAMides) is a possible ideal family of ligands to target this objective: being dianionic, they could potentially stabilize the high oxidation state of the metal and force it into a low coordinate geometry. 2-(2,6-dimethyl)-phenylamino-N-(2,6-dimethyl)-phenylbenzamide (figure 4) has been previously synthesized in our lab according to a two-step protocol [4]: this project aims to extend the ligand family and optimize the synthetic pathway and to react the ligands with Co, Ni and Cu to get the desired low-coordinate precursors to the desired oxidants (figure 5). The project entails organic synthesis, inorganic synthesis under inert conditions and eventually the use of different low-temperature spectroscopic techniques to study the reactive species.



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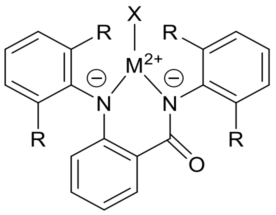

R=H, Me, iPr
M=Co, Ni, Cu
X=OAc, Cl, OTf

5

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Preparation and Characterization of Ni(III)/Cu(III)-Halide Complexes and Their Oxidative Reactions Towards Phenols and Hydrocarbons

Prof. Aidan McDonald (AMcD2)
aidan.mcdonald@tcd.ie

The oxidative functionalization of inert C–H hydrocarbons is an important transformation in biological systems as well as industrial catalysis. 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 M=O and M-OX (OX = OH, OR, O_2C-R, ONO_2). However, the HAT reactivity of the metal-bound halide in C–H/O-H activation has rarely been studied.

The major objective of this project will be to prepare a series of metal-halide (Ni, Cu) complexes incorporating *N,N'*-(2,6-dimethyl/ethylphenyl)-2,6-pyridinedicarboxamide (**L1, L2**) and N^2, N^5-bis(2,6-dimethylphenyl)-1H-pyrrole-2,5-dicarboxamide (**L3**) ligands (**Figure 1**) and investigate the reactivity of the corresponding high valent M(III)-halide complexes towards phenols and hydrocarbons.

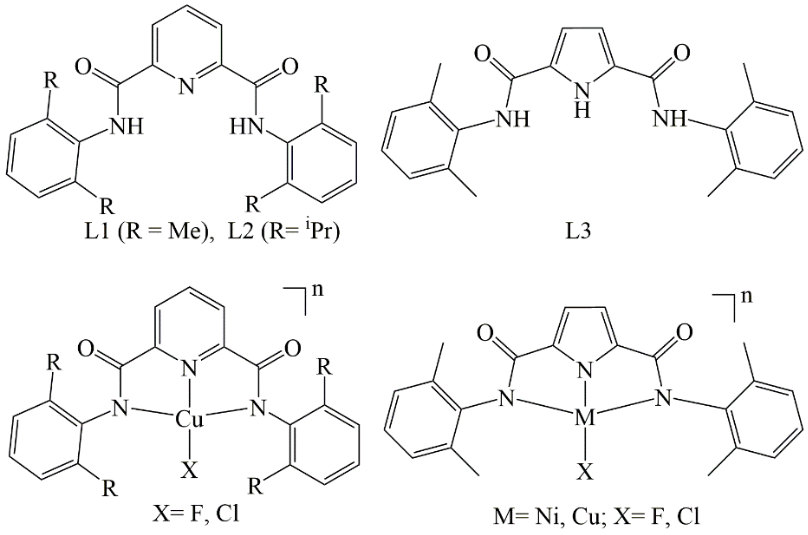

Figure 1. Representation of ligands and complexes.

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Biomimetic Dinuclear Copper Complexes and Their Reaction with Superoxide

Prof. Aidan McDonald (AMcD3)
aidan.mcdonald@tcd.ie

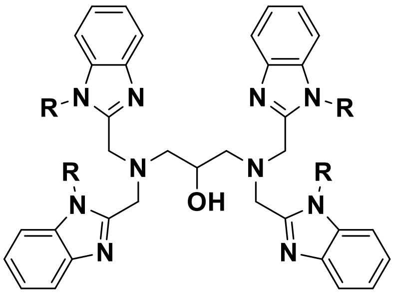
Oxidative stress plays an important role in a wide range of neurodegenerative diseases including Alzheimer's and Parkinson's disease, as well as in the aging process.[1] The oxidative stress is caused by an imbalance between the generation of reactive oxygen species (ROS) namely superoxide, hydrogen peroxide and hydroxyl radicals and the metabolism of these toxic compounds. ROS are naturally produced during oxygen metabolism.[2] Lipid peroxidation, protein oxidation and DNA damage in cells increases due to oxidative stress caused by ROS.[3]

The synthesis of model complexes capable of activating O_2 has become a big research area as it gives a better understanding of how metalloproteins function. Another oxidant found to play an important role in metalloenzymes is superoxide anion ($O_2^{\cdot-}$), a cellular free radical. In biology mononuclear non-heme iron enzymes such as superoxide dismutase (SOD), superoxide reductase (SOR) catalyse the reduction of superoxide [4,5].

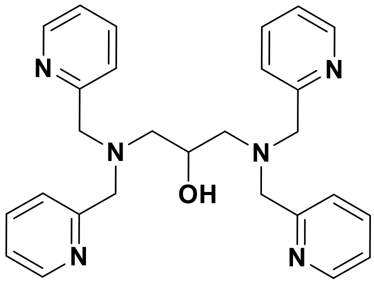
Copper is one of the most abundant transition metals in biological molecules. Copper is found in several proteins and enzymes involved in a variety of biological process such as respirations and protection against oxidative stress.[6] Catechol oxidases (COs) are dicopper metalloproteins responsible for the two-electron oxidation of o-diphenols to their corresponding quinones.[7] We have recently reported the nucleophilic reactivity of a Copper(II)-superoxide complex.[8] We are interested in investigating the reactivity of dinuclear copper complexes with superoxide.

The **major** objective of this project is to synthesise dinuclear Cu complexes based on the HPTB and HPTP ligand framework (see below figure) and investigate their reactivity towards KO_2.

Expected outcomes: Characterization of the synthesized dinuclear copper complexes by NMR, Mass-Spectrometry, UV-Vis and EPR. . The low temperature reactivity of these complex towards superoxide at -80°C will be investigated by UV-Vis spectroscopy. The results obtained will help us understand how metalloenzymes that contain dinuclear metal sites activate and react with superoxide.



HPTB



HPTP

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

Dr. Parvaneh Mokarian (PM1)
mokariap@tcd.ie

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 [1]. 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.

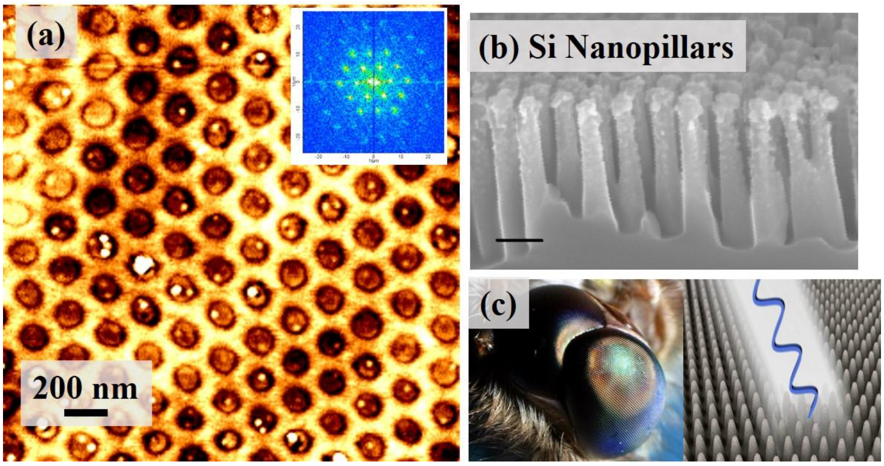

Figure 1. AFM topography image of (PS-*b*-P2VP), (b) Si Nanopillars synthesized using PS-b-P2VP as a mask mimicking moth eye (c).

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 [2]. 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.

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Study and measurement of reflectivity tailored by surface structuring

Dr. Parvaneh Mokarian (PM2)
email: mokariap@tcd.ie

The reflectivity of a material (such as glass) is set by its refractive index. To reduce reflectivity in applications such as glare on computer or phone screens thin films of lower refractive index are coated onto the surface. Reductions can alternatively be achieved by patterning the surface—i.e., etching pillars into the surface—with sub-micrometre size structures, one advantage of which is its applicability to a range of materials (see figure 1(a)) [**1, 2**]. Control over the pillar height, diameter and spacing/periodicity provides tuning of the material's reflectivity (see figure 1(b) and (c)) [**3**]. The fabrication of these structures will be performed separately within the group of Dr. Mokarian.

This project will focus on designing and subsequent measurement of patterns on glass which produce low and high reflectivity and, time permitting, other materials. Certain other applications of these patterned surfaces may also be studied (e.g., metasurfaces and plasmonic crystals). The outcomes for the student will be to learn suitable measurement techniques—depending on the materials measurements of transmission, reflection, scattering, absorption will be required—while some computational and analytical modelling may also be learned.

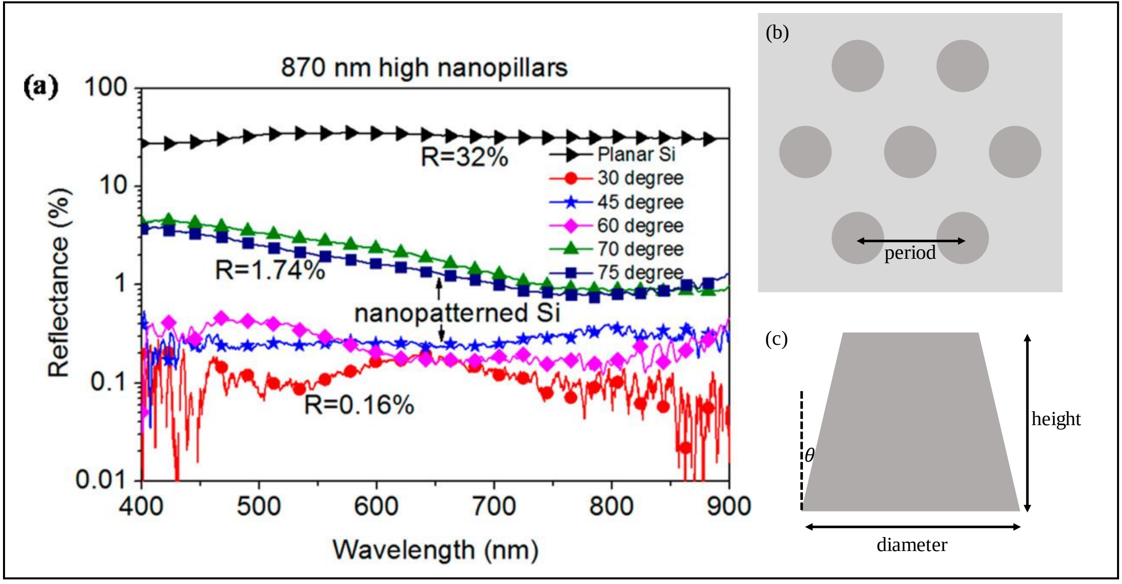

Figure 1. (a) Reduced in reflectivity of silicon achieved by patterning the surface [**1**]. Schematic of patterns in the surface looking (b) down on the surface and (c) at a cross section of a single pillar.

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Towards H_2 Economies: 4th Generation Metal-Organic Frameworks for Photo/Electro-Catalytic Device Fabrication

Prof. Wolfgang Schmitt (WS3)
schmittw@tcd.ie

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.[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.[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.

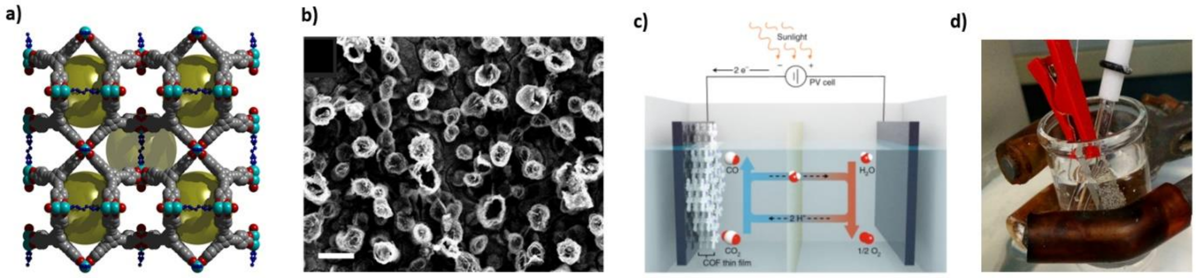

Figure: a) Crystal structure of catalytically active MOF; b) MOF grown on ITO electrode (SEM micrograph); c) Electrochemical cell setup; d) Catalytic water oxidation using MOF/ITO electrode.

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.

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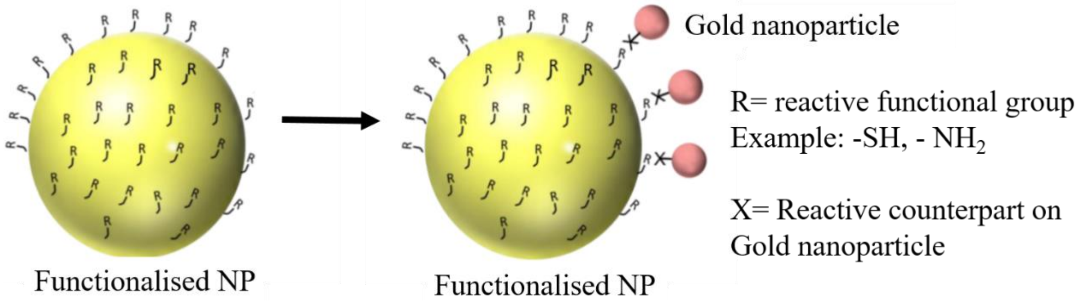
Surface reactive site mapping of functionalized Silica nanoparticles

Dr. Steffi Thomas (ST1)
Room 3.01, Main Chemistry building
ssthomas@tcd.ie

Research Project Description:

The surface functionalization of nanoparticles (NP) with specific groups and small molecules is an extremely important first step for most applications in nanomedicine, drug delivery and catalysis. The functionalisation is used to introduce various reactive groups and novel characteristics to the surface, to provide more compatibility between other nanoparticles, proteins to stabilize the NPs and significantly important to create reactive site to conjugate various further molecules like antibodies, enzymes, and therapeutic agents [1]. Organofunctional alkoxysilanes such as aminosilanes and mercaptosilanes are used mainly for introducing terminal amino and thiol groups, respectively on most metal oxide nanomaterials, thiolated ligands are used for gold surfaces etc.

The aim of the project is to investigate and understand the functionalisation of Silica nanoparticles (SiNPs) using thiol and/or amino functional groups [2,3]. These functional groups will be further characterised with photometric assays and mapped with specific gold nanoparticles to understand the spatial integrity of the reactive groups [4].



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Physical, Computational and Materials Chemistry

2D TMD modified membranes for filtration Applications

Dr. Ramesh Babu (RB1)
babup@tcd.ie

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 TMDs like liquid exfoliated MoS_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_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_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_2 based membranes for filtration applications.

Investigating the performance of cross-flow electro membrane filtration using charge selective nanofiltration membranes

Dr. Ramesh Babu (RB2)
babup@tcd.ie

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 exist 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. The study 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.

Fabrication and Testing of Random Nanowire Network Neuromorphic Devices

Prof John Boland (JJB1)
jboland@tcd.ie

Research Project Description:

Recent studies point to the presence of emergent connectivity paths in electrically addressed random nanowire networks [1]. The wires that comprise these networks have a metallic core with an outer layer of dielectric (oxide, polymer or molecular) that is a few nanometres in thickness. The junctions formed by these wires within networks can be switched on electrically and the network conductance Γ_{nt} scales with the current I passed through the junction (see Figure 1) where a single path emerges in (c) . Simulations also point to the possibility of building logic devices via a learning protocol that involves addressing a network through a combination of inputs and then monitoring the network response via a combination of outputs.

The student involved in this project will gain experience in spray-depositing networks, use a range of metal deposition techniques to make electrical contacts to these networks and will gain experience with the electrical testing procedure necessary to assess the logic performance. The student will work as part of a larger team and will be encouraged to develop new network layouts for different types of logic gate operations.

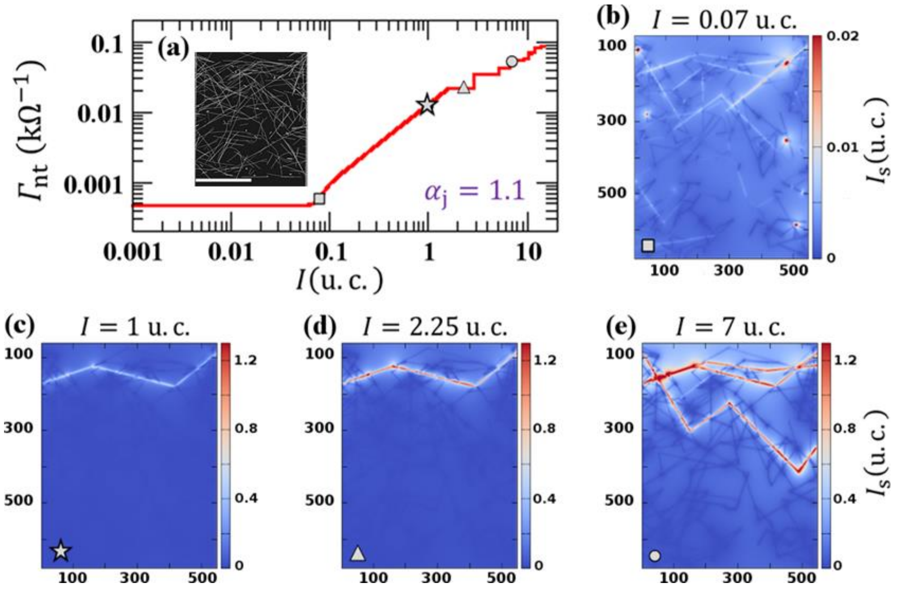

Figure 1 Simulated conductance evolution of an Ag nanowire network (NWN) vs applied current together with the conductance maps at different applied currents. Inset shows the simulated network, scale bar is 10 µm.

References

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Nanoscale Etching and Processing of Metal Surfaces

Prof John Boland (JJB2)
jboland@tcd.ie

Research Project Description:

Although metals were the first materials discovered by man, they remain key to our future sustainability. Improving the electrical resistivity of metals is critical: electrical resistance losses during power distribution can account for up to 20% of all electrical energy production and power dissipation in nanoscale interconnects represent a fundamental limitation on the device performance and battery life of all mobile devices. In this project the controlled etching and passivation of nanocrystalline copper films will be studied. Scattering from surfaces and grain boundaries are known to make important contributions of a metal's resistivity. The objective is to study the evolution of the surface morphology and resistivity following controlled oxidation, chemical etching and annealing, including the impact surface roughness and the grain boundaries present in the material.

The project involves using AFM to characterize the evolution of the nanoscale film morphology. The student will gain a comprehensive understanding of the AFM technique, including imaging modes and different approaches to materials processing and precision electrical measurements. The student will also receive an introduction to atom-resolved STM (see Figure 1). S/he will work as part of a larger team to help provide a fundamental understanding of behavior of nanoscale metals and the potential for engineering of lower resistivity materials.

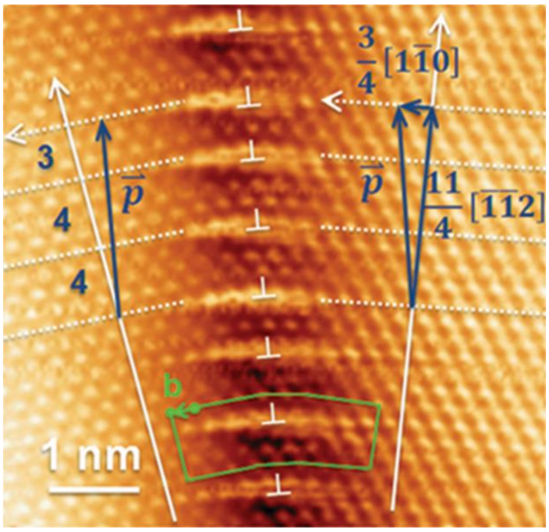

Figure 1 STM image of the boundary between two grains on the surface of a nanoscale copper film. The film normal orientation if [111] and the angle between the grain is about 16 degrees.

References:

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Sustainable materials for new energy technologies

Prof. Paula E. Colavita (PEC1)

Chemistry Extensions, tel. 3562; colavitp@tcd.ie

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.[1,2] 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. O_2, H_2O_2).

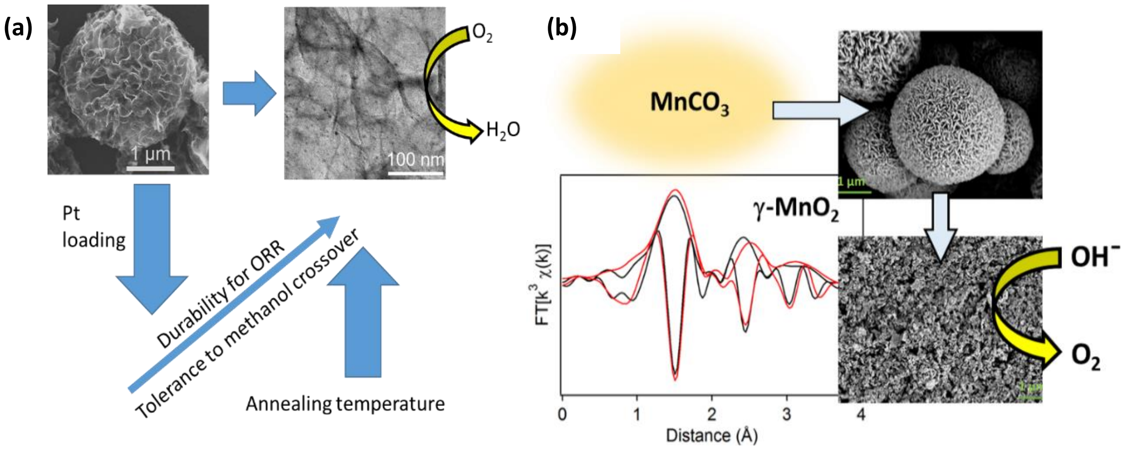

Figure1. (a) Carbon nanostructured microspheres for stable and methanol tolerant Pt-nanoparticle catalysis; these materials catalyse the oxygen reduction for methanol fuel cells [1]. (b) Nanostructured MnOx microspheres obtained via hydrothermal synthesis; these materials catalyse the oxygen evolution reaction that is essential in water splitting [2].

References:

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Plasma Treatments of Transition Metal Dichalcogenide Thin Films

Dr. Niall McEvoy (NM1)
CRANN 2.21; e-mail: nmcevoy@tcd.ie

Layered inorganic 2D transition metal dichalcogenides (TMDs), such as MoS_2 and WS_2 have attracted great research interest due to their potential applications in catalysis, (opto)electronics and sensing[1]. Due to their all surface nature, modifying the surface of 2D TMDs, through chemical functionalisation or defect engineering, has a profound effect on their properties and can be used to tune their performance to best suit specific applications[2].

While much work has focused on the use of wet chemical means to functionalise TMDs, with different functionalisation routes detailed[3], plasma treatments offer a thus far less explored route to tailor the properties of TMD layers. Plasma treatments offer a controllable means for the introduction of vacancy or defect sites, which can act as active sites for electrocatalysis or as a platform for further functionalisation. Furthermore, depending on the gas mixture chosen, plasma treatments can be used to introduce dopants in the TMD lattice.

Within this project students will first synthesise TMDs by chemical vapour deposition (CVD) using recipes established in the ASIN group[4]. These CVD-grown layers will be subjected to controlled treatments using a custom-built downstream plasma source. Their properties will then be investigated using Raman, photoluminescence and X-ray photoelectron spectroscopy. The suitability of these treated layers for applications in electronics and/or electrocatalysis will be investigated.

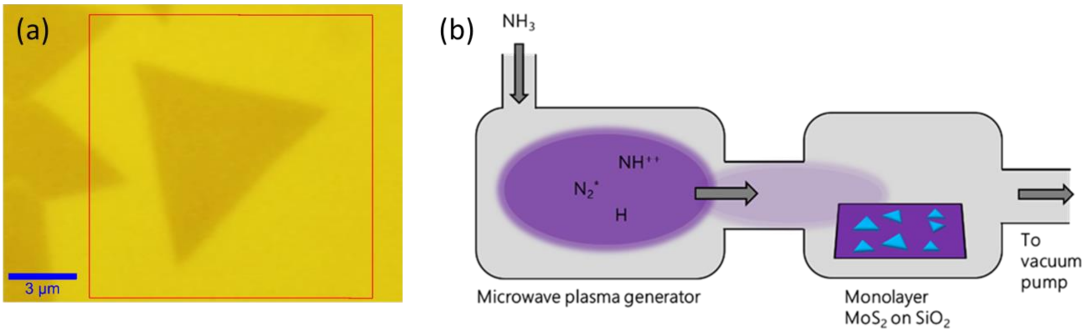

Figure (a) Optical micrograph of CVD-grown monolayer WS_2 (b) Schematic of downstream plasma treatment system.

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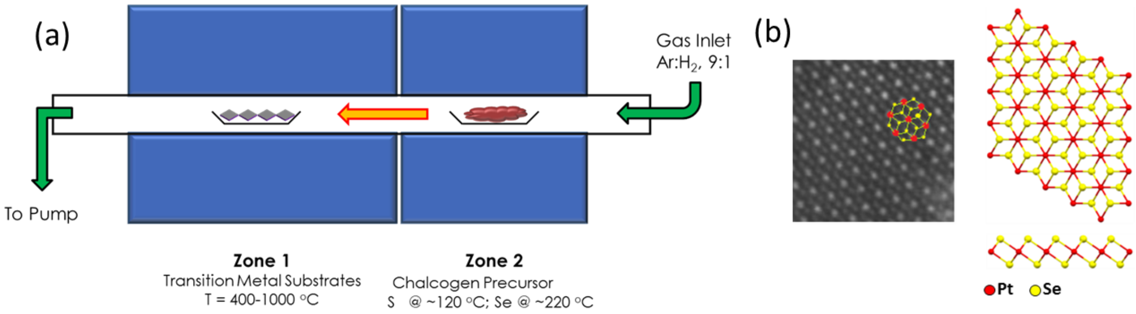
Low-Temperature Synthesis of 2D Transition Metal Dichalcogenides

Dr. Niall McEvoy (NM2)
CRANN 2.21; e-mail: nmcevoy@tcd.ie

2D transition metal dichalcogenides (TMDs) are inorganic materials composed of layers of metal atoms sandwiched between two layers of chalcogen atoms, with an MX_2 stoichiometry (M=transition metal, X=chalcogen, e.g. S, Se, Te). Their range of interesting properties mean that these materials have been touted for use in a wide range of applications[1]. However, the best route to their scalable synthesis in an industry-compatible manner is still a matter of much debate.

One of the synthesis routes investigated in the ASIN group is thermally assisted conversion (TAC) of predeposited metal layers in a chalcogen environment[2]. While most research efforts to date have focused on Group VI TMDs, such as MoS_2 and WS_2, recent reports have outlined the practicality of synthesing other TMDs, such as $PtSe_2$, by such methods[3, 4]. Importantly, this recent work was done at a relatively low temperature, meaning it is potentially suitable for certain industry processes. Initial work in the ASIN group has shown that other relatively unexplored TMDs, including PtS_2, SnS_2 and $SnSe_2$, can be grown by analogous methods at similarly low temperatures. Within this project, the synthesis of some of these materials will be investigated by TAC methodologies. Parameters such as pressure, temperature and precursors, will be optimized such that the material can be reliably reproduced with minimal contamination and with control over thickness and lateral size. The TMDs grown will then be characterized using Raman spectroscopy, X-ray photoelectron spectroscopy and electron microscopy. Time permitting; the materials will then be integrated into devices using micro-fabrication techniques available in the CRANN institute.



<u>Figure</u> (a) Schematic of TAC Growth of TMD layers. (b) HRTEM and crystal structure of TAC-grown $PtSe_2$.

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Fabrication of Two-Dimensional Heterojunctions

Dr. Niall McEvoy (NM3)
CRANN 2.21; e-mail: nmcevoy@tcd.ie

Our world relies on combinations of materials and the interactions between them; very rarely does a material provide any useful function in isolation. It is no surprise that soon after people developed an interest in two-dimensional (2D) materials, their focus turned towards combining them in novel ways with a view to real-world applications.

Consisting of layers of atoms less than a nanometre thick, 2D materials have a huge range of interesting physical and electrical properties leading to an explosion of research in the area. To date, the primary way to combine 2D materials has been to manually transfer an atomically-thin flake of one material on top of another to create heterojunctions. Needless to say this process is in no way scalable – and the interfaces between the constituents are imperfect.

In the ASIN group we investigate growing and combining these 2D materials using chemical vapour deposition[1]. We primarily work with graphene and semiconducting inorganic transition metal dichalcogenides (TMDs)[2,3]. This project will expand upon ongoing work in fabricating heterojunctions through *in-situ* growth[4]. A number of TMD combinations will be investigated. The heterojunctions will be characterised 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 heterostructures formed. All of this will take place using the equipment available in the ASIN group labs in CRANN.

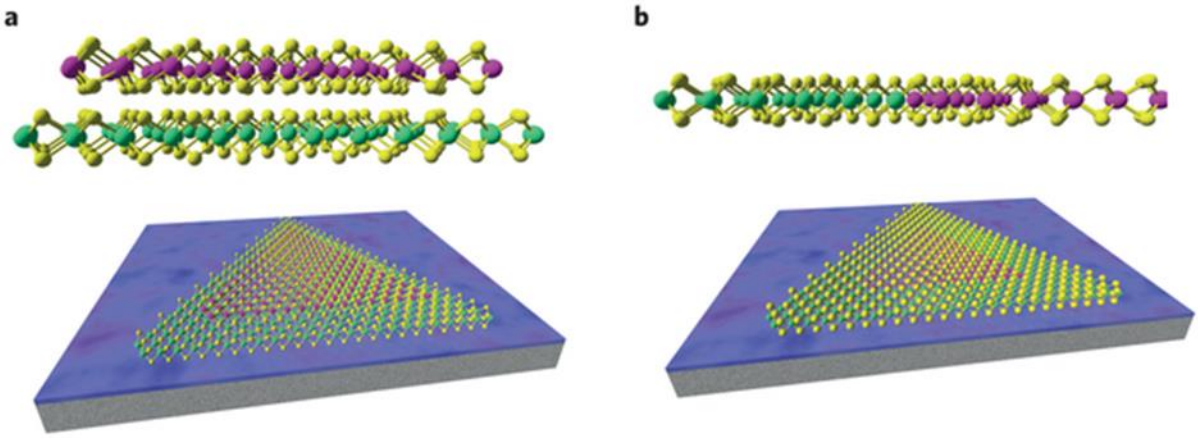

Figure Schematic of (a) vertical and (b) lateral TMD-TMD heterojunctions[4]

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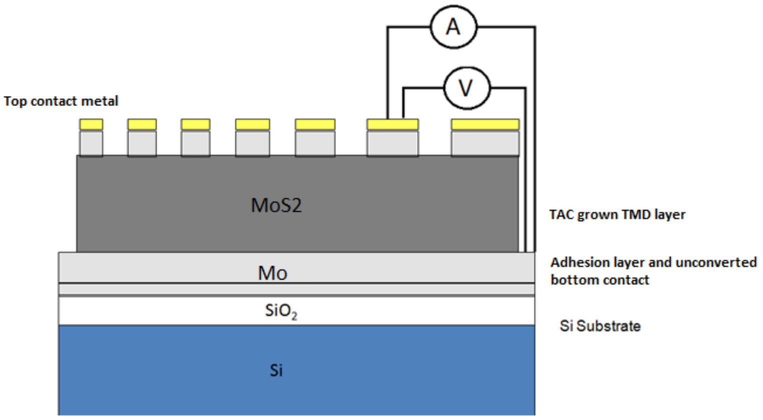
Investigation of the Thermoelectric Properties of 2D Transition Metal Dichalcogenides

Dr. Niall McEvoy (NM4)
Dr. Graeme Cunningham
CRANN 2.21; e-mail: nmcevoy@tcd.ie

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] which will then be tested thermoelectrically using charge coupled device thermoreflectance (CCD-TR).[3] 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_2Te_3 are most often employed as a solid solution, alloyed with isoelectronic Sb_2Te_3 and Bi_2Se_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 here, if time permits the two best power-factor materials may be paired and fabricated as a solid solution alloy.



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Monitoring chemical transformations on plasmonic nanoparticles by Raman spectroscopy

Dr. Richard Hobbs (RGH1)
Office 2.21 CRANN; email:hobbsr@tcd.ie

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 the cross-linking process in-situ while the structures are simultaneously 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.

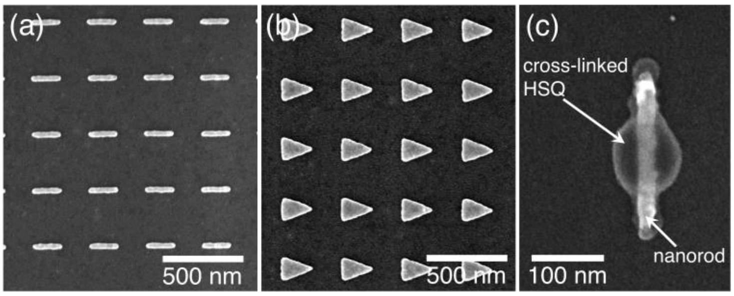

Figure 1. (a,b) Scanning electron microscope (SEM) images of Au nanorods and nanotriangle antennas fabricated by electron-beam lithography. (c) SEM image of localized region of cross-linked HSQ at the centre of a Au nanorod after illumination with a laser that is spectrally matched to the surface plasmon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

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Synthesis of heterostructured plasmonic nanoparticles

Dr. Richard Hobbs (RGH2)
Office 2.21 CRANN; email:hobbsr@tcd.ie

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 lithography[3] will be used to drive dissociation of precursor compunds, which will be prepared as thin films or 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. The project may also provide the opportunity to contribute to the construction of a new setup for the characterization of catalytic performance.

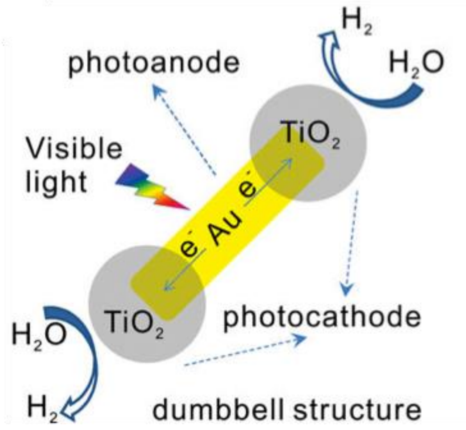

Figure 1. Schematic of a Au-TiO_2 heterostructured nanoparticle operating as a catalyst for hydrogen evolution.[1] In this work, plasmon-enhanced fields will be used to drive precursor decomposition in the desired locations to produce heterostructures with morphologies suited to catalyst function.

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Developing inorganic resists for helium-ion-beam lithography

Dr. Richard Hobbs (RGH3)
Office 2.21 CRANN; email:hobbsr@tcd.ie

The production of nanoscale patterns in ultrathin membranes lends itself to a variety of applications including electron optics, nanopore fabrication for DNA sequencing and water purification, x-ray optics and the advancement of optoelectronic devices. Moreover, as features on photomasks used in industrial optical lithography for the production of microelectronics continue to scale to smaller dimensions, advances in nanoscale patterning of ultrathin membranes becomes increasingly important. Consequently, the production of high-density patterns with sub-10-nm critical dimensions in ultrathin membranes will be the focus of this research project.

Charged-particle beams (electron/ion beams) have been used to directly pattern membranes by dislocating atoms in materials resulting in nanoscale milling or local changes in material composition.[1–3] Scanning transmission electron microscopes (STEMs) for example, have been used to produce holes with nanometer diameters in silicon nitride membranes for use as nanopores in electrochemical DNA sequencers. Similar approaches have been used to generate nanopores in graphene. Inorganic resists composed of low-*Z* materials such as Al_2O_3 and LiF have also been developed for patterning by electron beams. These resists are referred to as ablation resists due to an exposure mechanism based on electron-beam-induced dislocations and they have been used to produce extremely high-density patterns. Helium-ion-beam lithography (HeIBL) has also been used to create features with sub-10-nm dimensions in thin films. Given the relative immaturity of HeIBL there are many opportunities to develop patterning capabilities on the sub-10-nm length scale with this technique, including the development of new resists for HeIBL and investigation of the resolution limits of this technique. The low velocity of helium ions compared to electrons with comparable kinetic energy suggests that they may not suffer as strongly from proximity effects that can limit resolution. Consequently, an investigation of the resolution limits of FHIB lithography on ultrathin membranes with a variety of resists will be the focus of the present work.

During this project the student will receive training in the use of electron and ion-beam microscopes. They will learn about the interactions of electron and ion-beams with matter as well as nanofabrication and characterization techniques that are relevant to careers in the microelectronics and optoelectronics industries as well as nanoscience research.

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Redox and Oxygen Evolving Properties of Hydrous Oxide Films on Iron/Nickel alloys

Prof. Mike Lyons (MEGL1)
melyons@tcd.ie

Research Project Description:

One of the grand challenges facing 21st century society is in finding a clean, reliable and sustainable fuel to meet ever society's increasing demands. Hydrogen fuel is one fuel which meets and exceeds these criteria. One method suitable for large scale generation of hydrogen is by the electrolysis of water, with molecular hydrogen being produced at the cathode. However, the large obstacle facing this method is in the large overpotential (energy requirement) associated which the oxygen evolution reaction (OER) at the anode. Over the past thirty years, considerable research effort has been devoted to the design, synthesis and characterization of OER anode materials with the aim of achieving useful rates of active oxygen evolution at the lowest possible overpotential, thereby optimizing the overall electrolysis process. Currently, the optimal OER anode materials are Dimensionally Stable Anode (DSA) type electrodes based on RuO_2 and IrO_2. Despite their excellent electrocatalytic performance, the high cost of these materials, particularly iridium, and their poor long term stability in alkaline solution renders their widespread commercial utilisation both uneconomical and impractical. In light of these limitations, the oxides of the first row transition metals offer a compromise solution. Although they possess inferior electrocatalytic activity for the OER, their relatively low cost and long term corrosion resistance in alkaline solution makes them attractive OER anode materials.

The project will consist of electrochemically generating catalytically active oxide films on nickel/iron alloys in alkaline conditions with the student using a variety of electrochemical techniques to study the redox and oxygen evolving properties of these oxide films. These techniques will be supplemented by surface characterization tools such as SEM. [1-5]

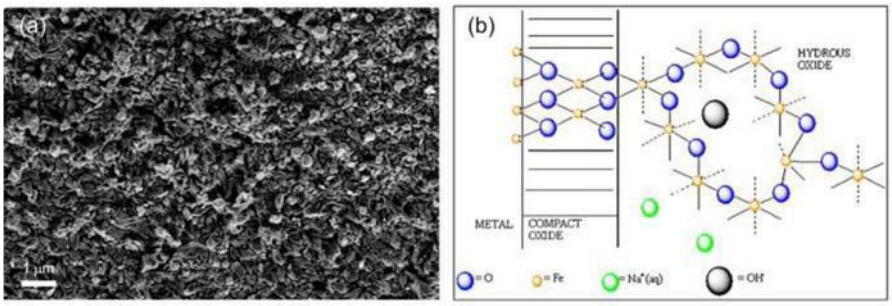

Figure 1 (a) SEM image of a hydrous oxide covered iron electrode. The film was prepared in 1.0 M NaOH for 120 cycles between −1.30 V and 0.75 V at a sweep rate of 400 mV s−1. (b) Schematic representation of the Burke- O‟Sullivan Duplex Layer Model of the oxide/solution interface.

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Electrochemical preparation and characterization of Cu-Ni microstructured alloys

Prof. Mike Lyons (MEGL2)
melyons@tcd.ie

Research Project Description:

Introduction: Copper-Nickel alloys are very important materials for a number of modern applications. They present high corrosion resistance in marine environment; the copper constituent gives high thermal and electric conductivity, whereas nickel presents magnetic and catalytic properties for water splitting reactions. Thus, Cu-Ni materials are potential good substrates for energy applications.

By using patterned electrochemical signals, the structure and composition of Cu-Ni materials can be controlled, which in turn determines its properties. It is thus possible to tailor performance by controlling the growing conditions, as necessary.

The objective of this project is to produce a systematic exploration of the relationship composition-microstructure-properties by using electrochemical methods.

Experimental techniques such as Cyclic Voltammetry, Chronoamperometry and Linear Sweep Voltammetry will be used to prepare the Cu-Ni substrates. Scanning Electron Microscopy, EDX and XRD will be used to characterize the morphology, local and global composition of the materials. Electrochemical properties in acid and base aqueous solutions will be evaluated with relation to water splitting reactions.

The expected outcome of this project is to produce a comprehensive relation between microstructure and the resulting properties of these important materials. These results will enlighten further advance in the area of green energy application and will be published in a peer-reviewed journal.

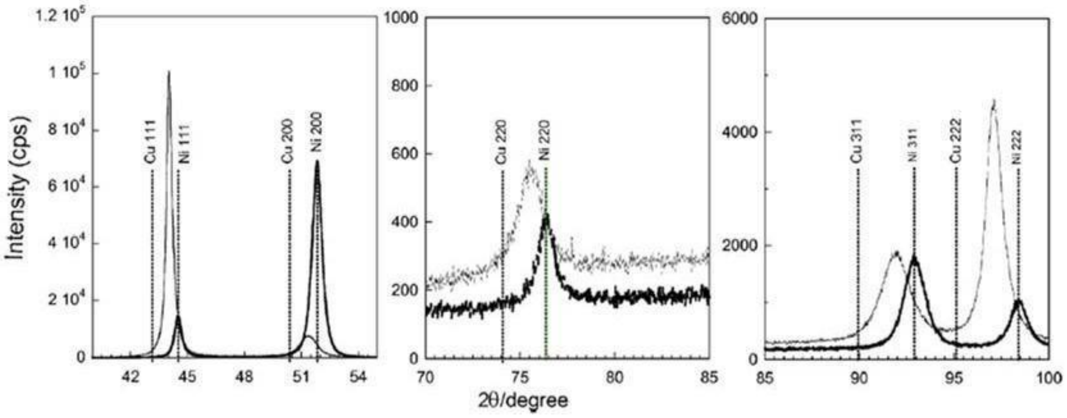

Figure 1: X-ray diffractograms (XRD) of deposits composed of pure Ni (black line) and Ni - 33% Cu (grey line). [*Taken from Ref. 3*]

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Bonding and Repulsion in Hydrogen Donor-Acceptor Pattern Recognition

Prof. Dónall A. Mac Dónaill (DMacD1)
E-mail dmcdonll@tdc.ie

Research Project Description:
The accepted role of hydrogen-bonding in nucleotide recognition has been questioned by Kool at 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].

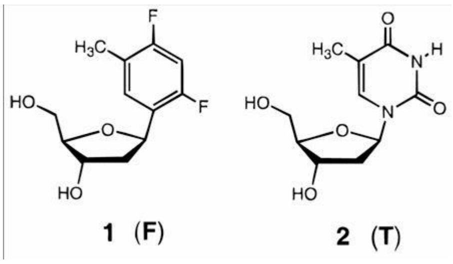

Figure 1. Difluorotoluene (F), a Nonpolar Isotere for Thymine (T) [2].

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.

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Tautomeric Instability and the Composition of the Nucleotide Alphabet

Prof. Dónall A. Mac Dónaill (DMacD2)
E-mail dmcdonll@tdc.ie

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.

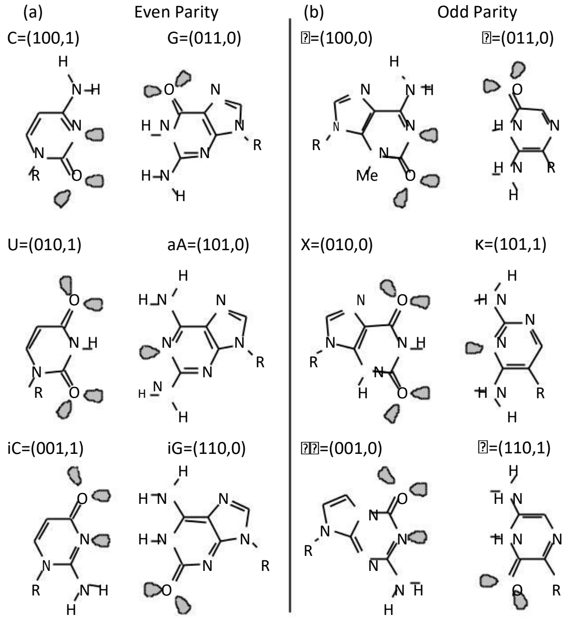

Figure 1. Potentially viable nucleotides divided by parity (a) the even-parity subset and (b) the odd- parity subset.

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.

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http://dx.doi.org/10.1038/343033a0

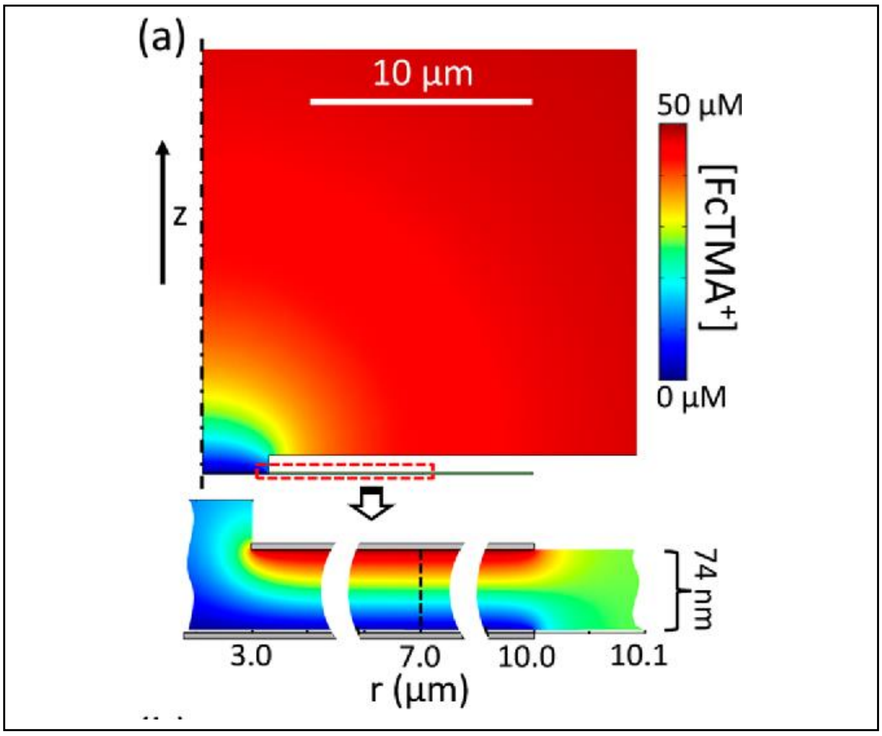
Dynamics of Redox Cycling in a Nanogap Electrochemical Cell

Prof. Kim McKelvey (KMcK1)

Kim.mckelvey@tcd.ie

A nanogap electrochemical cell can be created by precisely separating two electrodes by 10 –100 nm, as depicted in Figure 1. When one electrode is held at an oxidizing potential and the second electrode at a reducing potential, a redox species is oxidized at the first electrode, transported across the nanoscale gap (by a combination of diffusion, migration and convection) and then reduced at the second electrode. The nanogap traps the redox species and allows the redox species to repeatedly cycle between the two electrodes, which leads to a greatly enhanced electrochemical signal, a process known as redox cycling.

Redox cycling in a nanogap electrochemical cell enables us to probe the electrical double layer that forms at the electrode surface, particularly in low supporting electrolyte solutions.[1] However, nanogap electrochemical cells are typically difficult to fabricate.[2] We will used polystyrene nanoparticles are nanoscale spacers between two electrodes, to generate a quick and simple nanogap electrochemical cell, and then use this cell to probe the dynamics of double layer formation upon redox cycling.[3]



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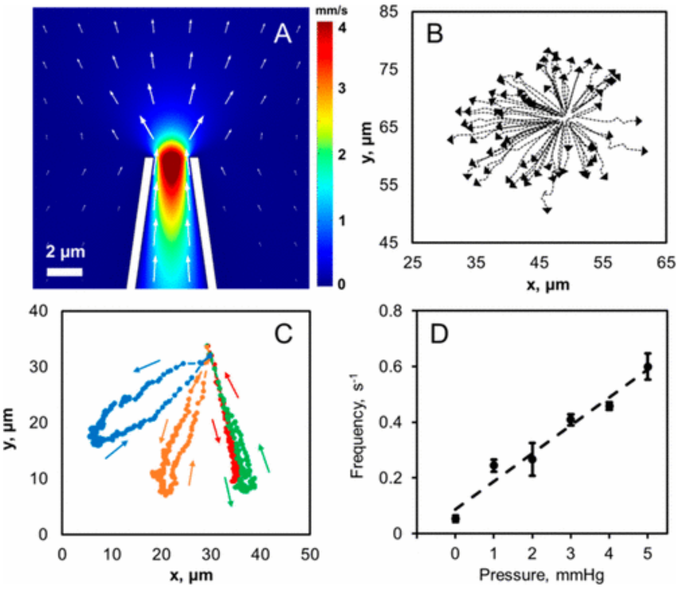
Single Nanoparticle Trapping

Prof. Kim McKelvey (KMcK2)
Kim.mckelvey@tcd.ie

Nanoparticles (particles with a radius < 100 nm) can be used for sensing applications, drug delivery, electrocatalysis and in energy storage technologies. Therefore, measuring the properties of individual nanoparticles is key to designing high performance nanoparticle-based technologies. However, isolating a signal from a single nanoparticle is extremely challenging, primarily due to the nanoparticles size.

One simple technique to isolate the signal from a single nanoparticle is resistive pulse sensing, in which the blockage of the ionic current through a nanopipette, as shown in the figure below, is used to detect a single nanoparticle as it passes through the opening. By reversing the force driving the nanoparticle a single nanoparticle can be moved repeatable back and forward, trapping it at the opening. By using a double barrelled nanopipette for the first time we will attempt to trap a single nanoparticle for many hours, enabling us to observe changes that occur to a single nanoparticle over the same time frame, such as single nanoparticle dissolution, single binding events, or changes in surface functionalisation.[1–3]

Goals:
1. Trap a single polystyrene nanoparticle using a double barrelled nanopipette.
2. Optimise trapping conditions to obtain > 2 hours trapping.
3. Measure the dissolution kinetics of a single polystyrene nanoparticle.
4. Optimise trapping conditions for Au nanoparticles.
5. Measure single molecule binding events on an Au nanoparticle.



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Molecular Catalysts for the Sustainable Production of Ammonia

Prof. Max García-Melchor (MGM1)

Lloyd Institute 2.31; garciamm@tcd.ie

Research Project Description

With a global production of 150 million tons in 2017[1], ammonia (NH_3) is regarded as a key chemical building block for the synthesis of most nitrogen-containing compounds with a vast range of applications including pharmaceuticals, propellants, and particularly fertilizers.[2] Despite this enormous demand, the industrial production of NH_3 still relies on the high-energy intensive and environmentally unfriendly Haber-Bosch process invented over 100 years ago, which requires high temperatures (*ca.* 500 C) and pressures (*ca.* 200 atm), as well as considerable infrastructure.[3]

Several earth-abundant transition metal catalysts have been recently shown to promote the catalytic conversion of N_2 to NH_3 (N2RR).[4,5] Motivated by these exciting findings, the proposed project aims to use density functional theory methods to shed light into the N2RR mechanism and the ligand effects observed with various earth-abundant transition metal catalysts. This project is expected to provide a fundamental understanding of the N2RR process at the atomic scale and to guide the future rational design of cost-effective and selective molecular N2RR catalysts. The project will be conducted in the Computational Catalysis and Energy Materials (CCEM) group led by Prof. García-Melchor, who will directly supervise the project.

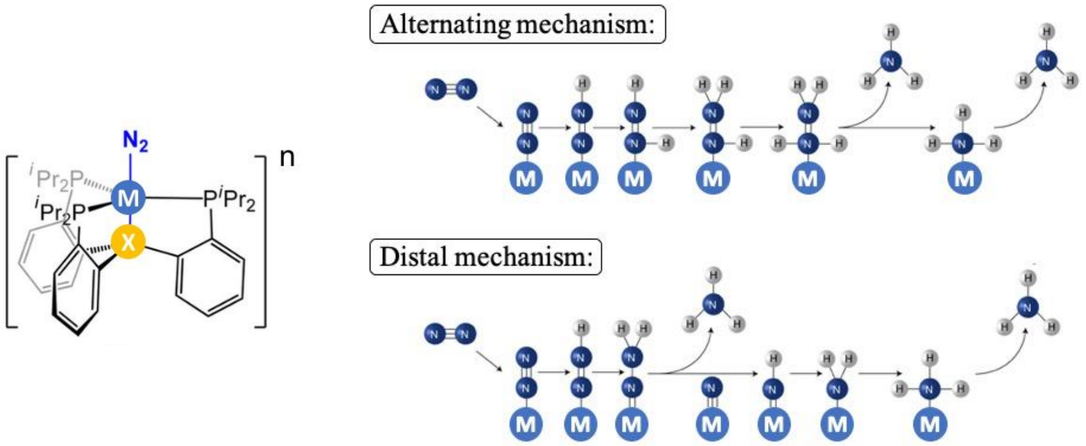

Figure: Model transition metal catalyst (left) and proposed reaction mechanisms for the N2RR (right).

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Modelling and Rational Design of Water Oxidation Electrocatalysts

Prof. Max García-Melchor (MGM2)

Lloyd Institute 2.31; garciamm@tcd.ie

Research Project Description

One of the biggest challenges of the 21st century is filling the gap between energy supply and demand with clean, reliable and inexpensive energy.[1] Renewable sources like those coming from sunlight or wind are potential alternatives but are limited by its intermittency, cost-effectiveness, and scalability. An alternative solution is to use the electrical energy generated from renewable sources to produce chemical fuels such as molecular hydrogen via electrochemical water splitting.[2] However, commercialization of devices based on this technology is hampered by the challenge in developing highly efficient and yet economic catalysts for the oxygen evolution reaction (OER) – one of the redox half-reactions in the overall water splitting process.

The proposed project will be conducted in the Computational Catalysis and Energy Materials (CCEM) group led by Prof. Max García-Melchor and aims to combine periodic density functional theory methods and linear scaling relations with the expertise of the group gained in previous works[3-5] to design cost-effective OER electrocatalysts.

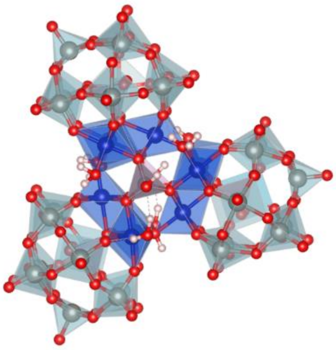

Figure: 3D-structure of a Co-based molecular OER catalyst.

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Mechanistic Study of the Selective Hydrogenation of Alkynes to Alkenes on 2D-Materials

Prof. Max García-Melchor (MGM3)

Lloyd Institute 2.31; garciamm@tcd.ie

Research Project Description

Alkyne semi-hydrogenation is one of the most widely studied reactions due to its primary role in the purification of rich olefin streams in oil refineries and its potential for the large-scale production of commodity chemicals such as ethylene.[1] This process is traditionally carried out by different formulations of Pd catalysts in combination with promoters such as lead or organic ligands.[2-4] Over the last decades, significant efforts have been made to develop non-precious metal catalysts that perform comparably to Pd. However, most of these materials are either less active or suffer from selectivity losses, namely over-hydrogenation and oligomerization.[4]

This original research project intends to explore the viability of 2D-materials based on Earth-abundant elements as novel catalysts for the semi-hydrogenation of alkynes to alkenes. With this aim, the candidate will be instructed in the use of periodic density functional theory methods to model the reaction intermediates and transition states involved in the hydrogenation of model terminal alkynes. This project will be carried out in the Computational Catalysis and Energy Materials (CCEM) under the direct supervision of Prof. Max García-Melchor.

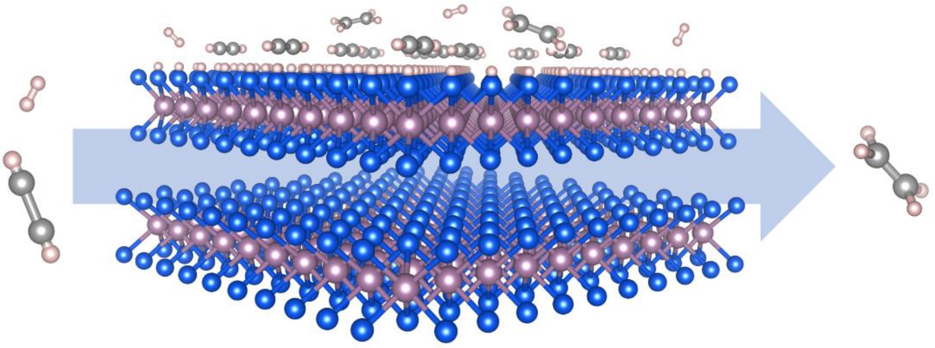

Figure: Structural model of a 2D-material as catalyst for the partial hydrogenation of acetylene.

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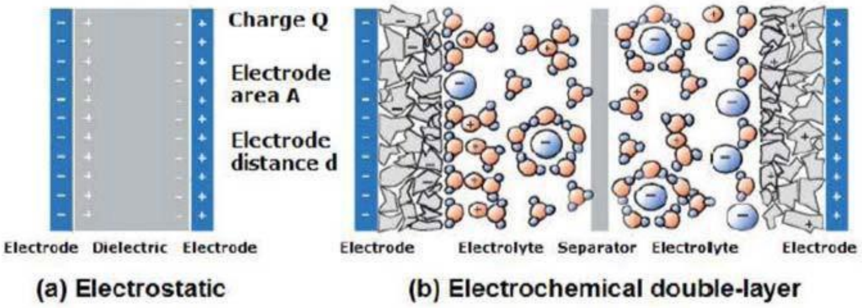
Development of ultra-thin energy storage devices based on two- dimensional nanomaterials

Prof. Valeria Nicolosi (VN1)

CRANN L2.19 / nicolov@tcd.ie

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 CO_2 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 nanomaterials[2-4] 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.



(a) Electrostatic (b) Electrochemical double-layer

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

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Doping Cu_2O – towards low cost photovoltaic cells.

Prof. Graeme Watson (GWW1)
Room LB 2.36, Email watsong@tcd.ie
http://www.tcd.ie/Chemistry/staff/people/gww/gw_new/

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 TiO2 through dyes, doping or co-doping have not succeeded in providing a viable material.

Cu2O was the first material for which a patent was granted for a photovoltaic material but despite its historical importance, Cu2O 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 Cu2O are present would need to be fabricated, [3] although currently no viable way of creating (through doping) n-type Cu2O has been found [4].

In this project we will use density functional theory to examine the defect chemistry of Cu2O 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 Cu2O (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.

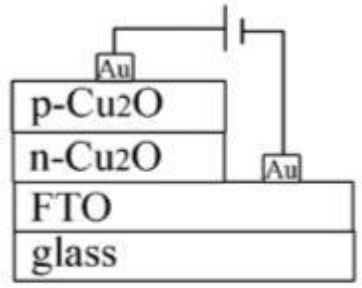

Figure 1. Schematic of a Cu_2O homojunction photovoltaic cell.

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Analyzing the electronic structure of a series on copper antimony sulfides.

Prof. Graeme Watson (GWW2)
Room LB 2.36, Email watsong@tcd.ie
http://www.tcd.ie/Chemistry/staff/people/gww/gw_new/

Research Project Description:

Most of the current industry standard oxide/chalcogenide semiconductors utilized in electronics/optical applications, display n-type conductivity. In this project we will investigate a range of ternary copper antimony sulfides [1] (CuSbS2, Cu3SbS3, Cu3SbS4, Cu12SbS12) as potential p-type conducting material for energy applications. We are especially interested in predicting materials which show both *n* and *p*-type ability (bi- polar ability), which can be easily made into functional diodes.

We will use state of the art *ab initio* modelling techniques to characterize these materials and predict the phase diagram, electronic structure (Electronic Density of State – EDOS), band structure, effective charges, effective electron and hole masses and optical adsorption to assess their suitability for semiconductor applications.

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Responsive Photonic Crystal Structures

Dr. Larisa Florea (LF1)
CRANN 4.12, Main Chemistry Building 1.04, ext 3086, floreal@tcd.ie

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 materials[3-5], with high-resolution 3D fabrication. In this context, structures will be fabricated from stimuli-responsive materials, using direct laser writing by 2-Photon Polymerisation[6] (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.

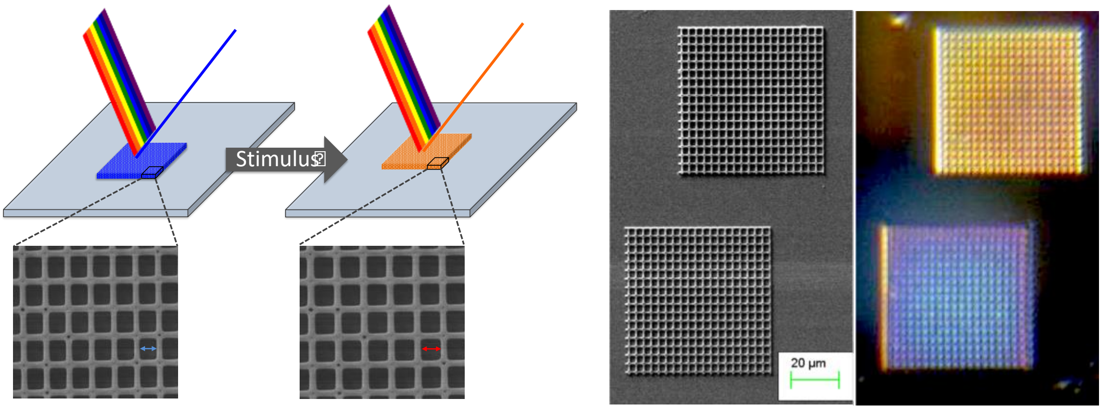

Figure 1. Photonic crystal sensor. (Left) Diagram depicting the working principle of the sensor. The sensor consists of stimuli-responsive 3D structure fabricated by direct laser writing. (Right) SEM and reflection microscopy images of the 3D structures fabricated by direct laser writing.

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Stimuli-responsive Hydrogel Structures

Dr. Larisa Florea (LF2)
CRANN 4.12, Main Chemistry Building 1.04, ext 3086, floreal@tcd.ie

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.[1-5] 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).

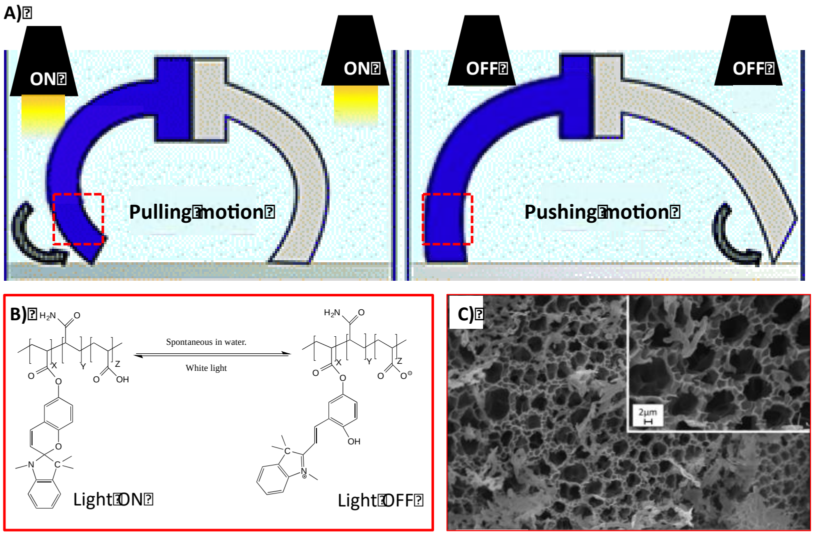

Figure 1. A) Schematic illustration of a photo-actuated hydrogel micro-walker; B) Chemical structure of the polymer used for the fabrication of the photo-actuated hydrogel micro-walker; C) SEM image showing the high porosity of the hydrogel material.

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