# SURE Projects and Supervisors 2014

(1) Shane Bergin Sticky Nanomaterials
(2) Werner Blau I Non-contact Raman Analysis of Historical Manuscripts
(3) Werner Blau II Carbon Nanotubes for Renewable Saline Power Generation
(4) Mike Coey Magneto-electric coupling in thin film stacks
(5) Graham Cross Fabrication of nano-porous patterns by nanoimprint lithography
(6) John Donegan I Conical refraction of light with spatial light modulation
(7) John Donegan II Simulation tools for plasmonic elements
(8) Paul Eastham Theory of quantum state control with solid-state qubits
(9) Brian Espey Tomography of light pollution
(10) Peter Gallagher Software Development for www.SolarMonitor.org
(11) Stefan Hutzler Experimenting with foams
(12) Matthias Moebius Bubble formation at gas-evolving micro electrodes
(13) David O'Regan Simulation of magneto-optical spectroscopy
(14) Ramesh Babu Functionalization of membrane surfaces
(15) Stefano Sanvito I Model of oxidation processes in solid oxide fuel cells
(16) Stefano Sanvito II Predicting new magnetic materials
(17) Stefano Sanvito III Tetragonal distorted Heusler alloys
(18) Stefano Sanvito IV Simulating the switching of a memory cell in STT-MRAM
(19) Wolfgang Schmitt Nanosized Clusters and Bio-Inorganic Network Structures
(20) Igor Shvets Atomic Force Microscopy Investigations of Vicinal Substrates
(21) Hongzhou Zhang Cathodoluminescence detection in the SEM

## Section 1 – Supervisor Details

**Name:** Dr Shane Bergin

**School:** Physics & CRANN

**Email:** berginsd@tcd.ie

## Section 2 – Project Details

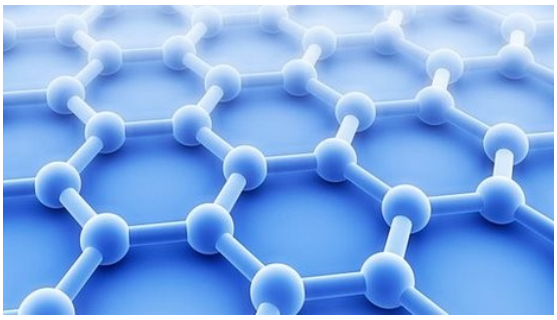
### Sticky Nanomaterials – What's the fuss?

### Project Description (500 words or less):

Whilst miniaturisation of materials is itself exciting, this is not what makes nanomaterials special. The properties of materials on the nano-level are influenced by both quantum phenomena (materials a few atoms big are can be described by many of the laws of atomic physics) and those of bulk materials; this unique combination is what drives research in nanoscience. Many of the nanomaterials of interest to science today, are nano-scaled in one or more of their three dimensions – these are known as low dimensional nanomaterials.

The properties of nano-materials such as carbon nanotubes, graphene, and other 2-dimensional nanomaterials are severely limited by their tendency to aggregate. Since 2006, Dr. Bergin has worked on methods to overcome this problem. His central finding, in this work, was that the degree of exfoliation for any nanomaterial could be optimised by matching the surface energy of the solvent to the surface energy of the nanomaterial.

Currently, Dr. Bergin and his team are investigating the surface energies of a range of nanomaterials using inverse gas-chromatography. The surface energies of most nanomaterials (and indeed bulk/starting materials like graphite) are poorly defined – this has consequences when trying to disperse them. Understanding what contributes to the surface energies of nanomaterials will allow tailored



dispersions of nanomaterials to be easily created. Inverse gas chromatography measures the surface energy of a material by passing a series of gases through the sample and looking at how they stick to the surface.

In this project, the student will use inverse gas chromatography to investigate the surface energetics of a range of novel two-dimensional materials. Does graphene's surface energy differ to graphite? Does the size of the graphene flake influence its surface energy?

The student will work closely with a team of research students from my lab as well as those in Prof. Coleman's lab.

## Section 1 – Supervisor Details

**Name:** Prof. Werner Blau / Dr. Susie Bioletti

**School:** Physics / Library

**Email:** wblau@tcd.ie / bioletts@tcd.ie

## Section 2 – Project Details

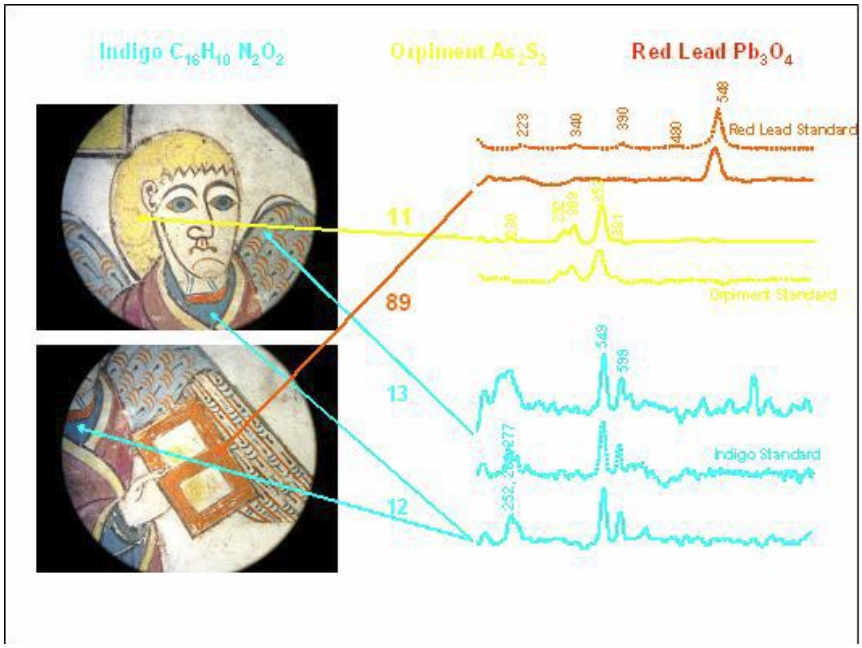
**Project Title** Non-contact Raman Analysis of Historical Manuscripts

**Project Description (500 words or less):**

This project arises from collaboration between TCD Library and the School of Physics which has already resulted in a comprehensive study of pigments used to illuminate the world-famous Book of Kells [1].
The identification of pigments, in particular the inorganic ones, used to illuminate historical manuscripts is most effectively carried out by Raman microscopy, a technique used widely in pharmaceutical and medical research. It has only been employed for pigment identification in the field of fine art in the past 15 years
Raman spectroscopy is a form of vibrational spectroscopy. Modern Raman spectroscopy involves the irradiation of a sample with laser light of a specific wavelength. By measuring the energy difference between the initial and scattered photons the characteristic vibrational frequencies of the pigment can be determined.
If the spectrum has sufficient definition it may be compared with known standards to give unambiguous identification. X-Ray Fluorescence (XRF) will compliment both of the above techniques by identifying specific elements present within the material and their relative proportions.
The manuscripts chosen for this project will be predominantly the 'Papyri' (Greek, 13$^{th}$ – 7$^{th}$ century B.C. http://www.tcd.ie/Library/manuscripts/collections/papyri.php). Time permitting, the Book of Dimma, Book of Mulling, and Garland of Howth (Irish, 8$^{th}$ century A.D.

http://www.tcd.ie/Library/manuscripts/collections/medieval-latin.php) will also be studied.

[1] Bioletti, Leahy, Fields, Meehan, Blau; J. Raman Spectr. 40 (2009) 1043



## Section 1 – Supervisor Details

**Name:** Prof. Werner Blau

**School:** Physics

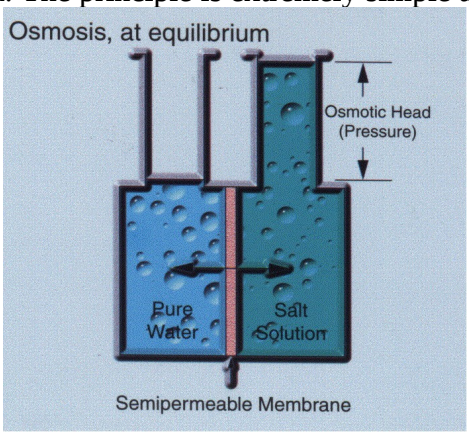
**Email:** wblau@tcd.ie

## Section 2 – Project Details

**Project Title** Carbon Nanotube Membranes for Renewable Saline Power Generation

## Project Description (500 words or less):

This project intends to demonstrate the scientific feasibility to employ Carbon Nanotube based sheets as membranes for efficient and renewable salinity power generation. In Pressure-Retarded Osmosis (PRO) , seawater is pumped into a pressure chamber where the pressure is less than the osmotic pressure difference between fresh water (or low salinity water) and seawater (or higher salinity water). Freshwater flows through a semi-permeable membrane and increases the volume (or pressure) within the chamber; a turbine is spun as the pressure is compensated. The principle is extremely simple and depicted here.




The performance of the membrane is crucial for the success of this technology and currently presents the major bottleneck for large-scale commercial feasibility of this technology. Current cellulose acetate membranes allow for very high water permeability,

but possess high salt permeability also. In order to generate a high head of pressure build-up, only high water permeability can be allowed.

Osmosis, exactly of the type used here, is common in biological systems. Aquaporine protein channels represent the best example for a biological effective semi-permeable membrane. They possess water transport properties of 51,000 $L/m^2h$ which is about 10,000 times more efficient that current synthetic membranes. State-of-the art high-performance synthetic cellulose membranes have water transport properties in the range 5 – 30 $L/m^2h$ only.

In this project, we intend to demonstrate the feasibility of using Carbon Nanotube (CNT) sheets as membranes for this purpose, to mimic and approach the performance of the biological membranes.

## Section 1 – Supervisor Details

**Name:** Prof. J. M. D. Coey/Dr. K. Rode

**School:** Physics

**Email:** jcoey@tcd.ie, rodek@tcd.ie

## Section 2 – Project Details

## Project Title: Magneto-electric coupling in thin film stacks

## Project Description:

Magneto electric coupling provides the possibility to switch the magnetisation of a thin film layer or bulk material by the application of an electric field or vice-versa. The coupling has so far been demonstrated in both thin films and bulk samples, but efficient switching has only been seen in bulk samples of $BiFeO_3$. [1]

In this project we propose to grow a multilayer stack composed of two ferromagnetic electrodes separated by a thin, insulating, ferroelectric layer. By applying a voltage between the two ferromagnetic electrodes, the electric polarisation of the insulator is controlled, and we aim to investigate the coupling between this polarisation and the magnetic state of the two ferromagnetic electrodes by measuring the tunnel magneto resistance (TMR) and the tunnel electro resistance (TER) of a patterned thin film device.

The student will be responsible for developing the growth process of the samples using pulsed laser deposition, characterisation of the structural and magnetic properties of the thin-film stack, as well as investigating the magneto-electric transport properties of the device.

In our preliminary measurements of an $La_{2/3}Sr_{1/3}MnO_3/BaTiO_3/SrRuO_3$ patterned stack, we have identified clear coupling between the magnetic state of the electrodes (anti-parallel or parallel) and the TER sign and value (see Figure 1).

**References**

**[1]** D. Lebeugle et al., Phys. Rev. Lett. 100, 227602 (2008)

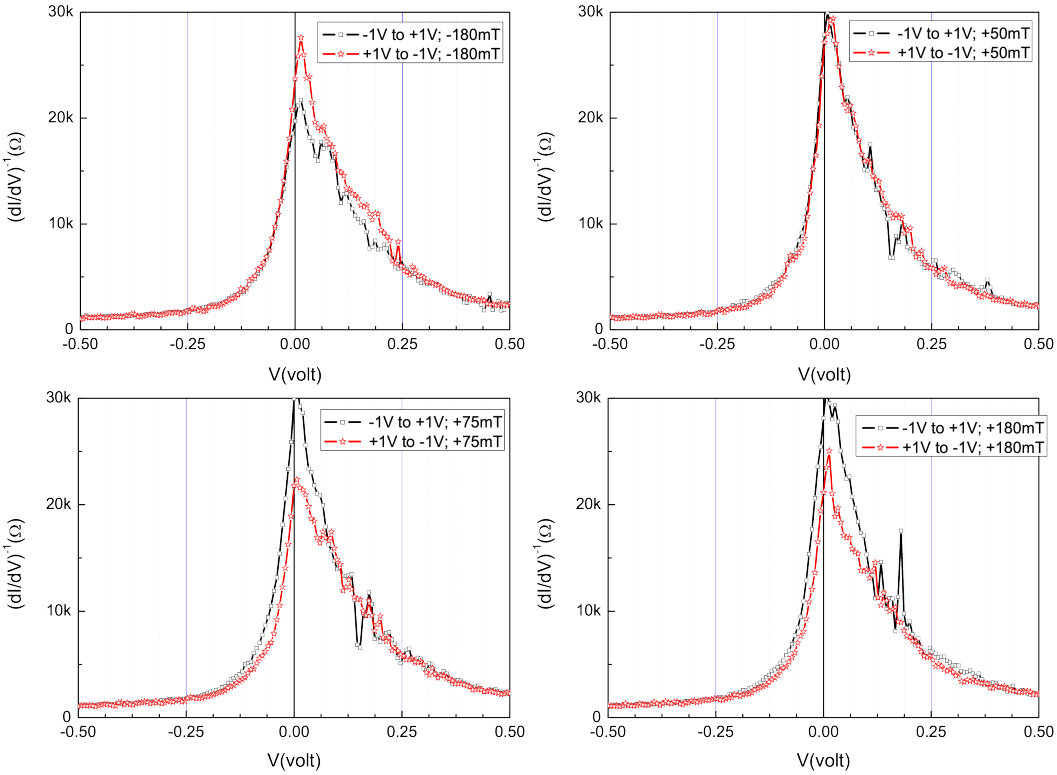



Figure 1: I(V) of an SRO/BTO/LSMO tunnel junction in an applied magnetic field of -180 mT, +50 mT (corresponding to the coercive field of the LSMO electrode), +75 mT and +180mT. Notice the sign change of the TER as a function of the applied magnetic field.

## Section 1 – Supervisor Details

**Name:** Dr Graham Cross

**School:** Physics

**Email:** crossg@tcd.ie@tcd.ie

## Section 2 – Project Details

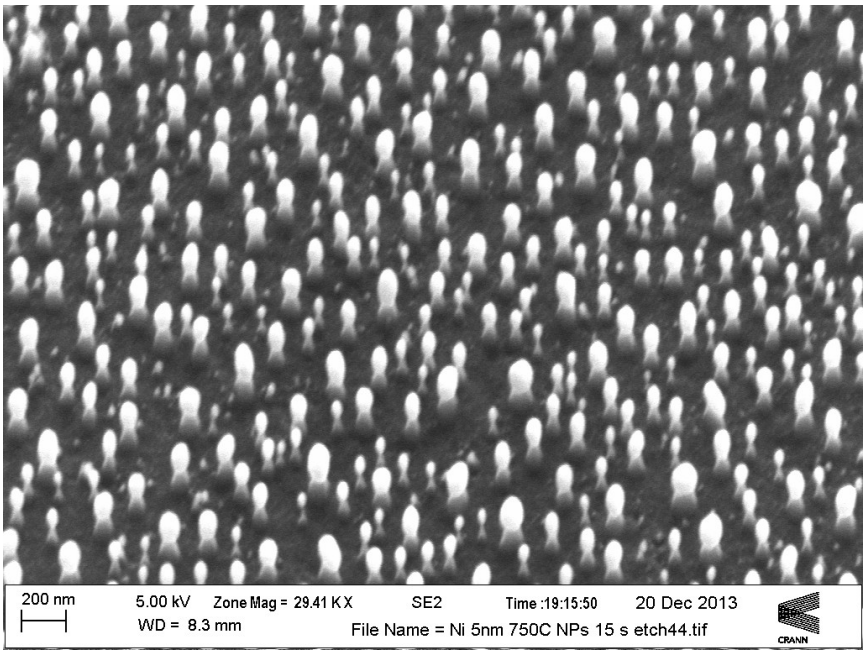
**Project Title: Fabrication of nano-porous patterns inside beer cans by means of nanoimprint lithography.**

**Project Description**: Nanoscale patterns can be used to provide specific functional responses and consumer experiences from food packaging including beer cans. Efficient fabrication of nanometre scale patterns in polymers has received significant attention in the past decade as a means to enable the development of future technologies. Due to their outstanding properties such as selectivity for surface modifications and alterable geometry nanopores materials have been used for a wide range of applications as well as for studying fundamental theories about nanoscale confinement. The nanoscale of features' dimensions and spacing and ability to control structure, dimensions and periodicity make nanoimprint lithography (NIL) an ideal technique for nonoporous polymer film fabrication.

Most important elements of the NIL technique are the stamp fabrication and the correct selection of the imprinting parameters. The first objective of this project is to design and fabricate the NIL stamps containing an array of nanopillars, 50-100 nm in diameter and minimum of 250 nanometres in height. Ultimately, the stamps are intended to be utilised in the room temperature stamping process which involves significant pressure load and requires mechanically strong stamps. Therefore, unlike in most applications, the stamps are intended to be fabricated of diamond-like-carbon (DLC) films, which brings certain requirements to the manufacturing process.

The proposed stamp nanofabrication process consists of three steps and allows for fabrication of high relief structures on nanoscale. The process begins with molecular bean epitaxy (MBE) deposition of 5-10 nm thick Ni film on top of a DLC surface followed by annealing at 700-900 °C. Due to the surface energy mismatch between Ni and DLC, the Ni film is expected to transform into well separated, 50-100 nm nanoparticles which will later serve as a shadowing mask in the subsequent DLC etching in the inductively couple plasma (ICP). Areas under the Ni nanoparticles shadowed areas are expected to transform into nanopillars due to the material removal around them. The film thickness, annealing temperature and time, ICP power and etch time would have to be optimized for the stamp fabrication process. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) will be utilised in the DLC surface characterisation.

Once the process is established and the stamps are ready, they will be imprinted into the polymer surface. Both, mechanical press and automated NIL instrument will be utilised in this work. The influence of the imprint parameters such as temperature, pressure and duration on the morphology and quality of the stamped polymer surface has to be established. AFM and SEM techniques will be used for the polymet surface analysis.




A diamond-like carbon (DLC) nano-imprint die

**Section 1 – Supervisor Details**

**Name:** Professor John Donegan

**School:** Physics

**Email:** jdonegan@tcd.ie

**Section 2 – Project Details**

**Project Title** Conical refraction of light with spatial light modulation

**Project Description (500 words or less):**

Conical refraction of light was discovered in Trinity College Dublin in 1832. William Rowan Hamilton predicted the phenomenon and later that year in a very challenging experiment, Humphrey Lloyd demonstrated conical refraction in a crystal of aragonite. In recent times, Professors Lunney, Eastham and Donegan have revitalised the research in this unique optical phenomenon. This new area of research has been allowed through the availability of very high quality biaxial crystals.

One of the important properties of the conical refraction beam, is the unique spatial profile which gives it the characteristic rings known in many experiments. The beam also possesses orbital angular momentum and this aspect of the beam will form this SURE project.

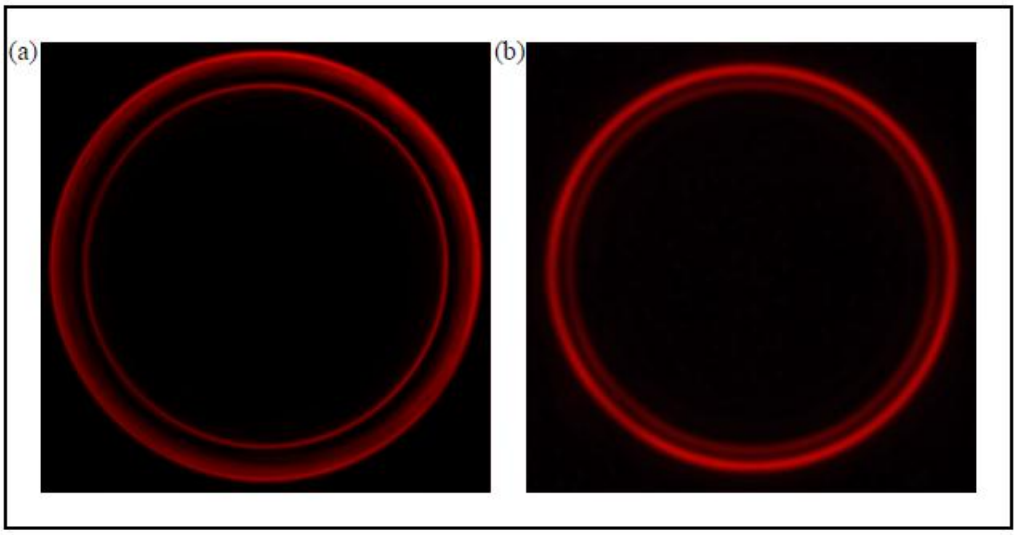



Figure: Ring profiles in conical refraction seen with (a) top-hat and (b) Gaussian beam profiles.

We will use a spatial light modulator (SLM) to analyse the phase distribution of the conical refraction beam. In addition, we can cascade two or more conical refraction beams and see how the phase profile change in such diverse geometries. Finally, we will study the very interesting case of a radially polarised beam and how conical refraction can be used in such a case.

The study will entail both experimental and modelling work.

**Section 1 – Supervisor Details**

**Name:** Professor John Donegan

**School:** Physics

**Email:** jdonegan@tcd.ie

**Section 2 – Project Details**

**Project Title** Simulation tools for plasmonic elements

**Project Description (500 words or less):**

Plasmonic systems are presently of very strong interest. In such structures, as they interact with light, the plasmon mode that is excited has a wavelength much less than that of light. There is much activity based on designs of plasmonic structures that will produce heating on the nanoscale.

There are many different methods to simulate plasmonic structures. The main ones are finite element modelling (FEM), finite difference time domain (FDTD) and discrete dipole approximation (DDA). Each of these have their realms of applicability and are very useful in designing such structures.

In this project, these various simulation tools will be examined with a number of different test structures including a linear taper, a metal-insulator-metal structure and a metallic helix. An example of a helix with FEM is shown in the figure below.

This project will be strongly focussed on simulation and will suit a student with a strong mathematical background.

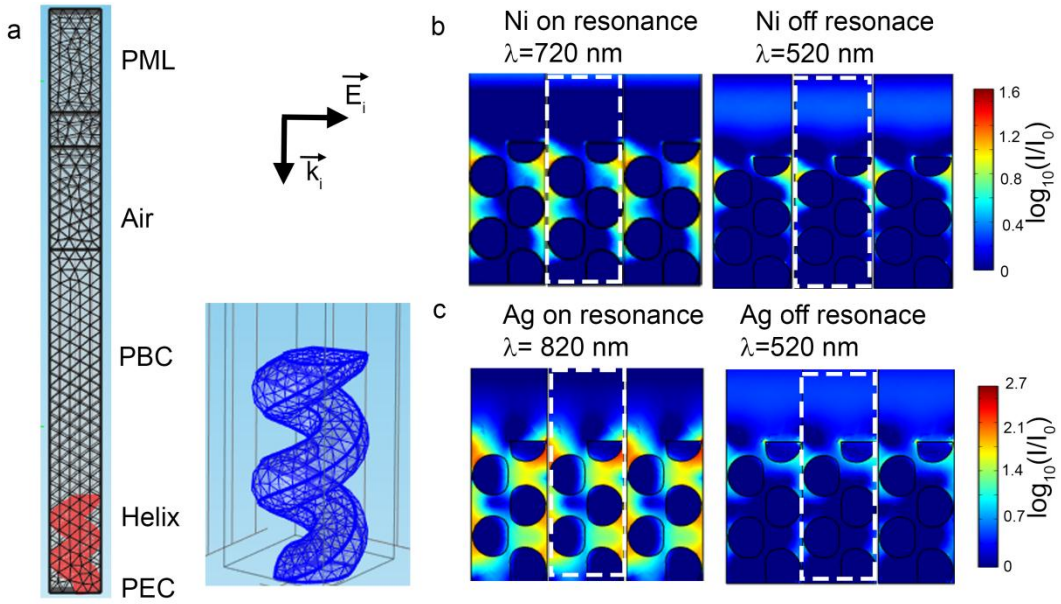



**Figure**. **FEM simulations of the nanohelix array. a** The domain and mesh used for the simulations. The largest element size used was 50 nm , which was decreased to 10 nm inside the helix. The incident field is normal to the surface and polarized in the y-direction. **b** Near field intensity normalized to incident intensity on a log scale in y-z plane for Nickel on and off a resonance. **(b)** same for silver.

Section 1 – Supervisor Details

**Name:** Dr Paul Eastham

**School:** Physics

**Email:** easthamp@tcd.ie

## Section 2 – Project Details

### Project Title

Theory of quantum state control with solid-state qubits

### Project Description (500 words or less):

The potential to exploit quantum-mechanics in technology, from sensors to computers, is vast. Essential for these developments, however, is the ability to take a quantum system with a few discrete states, such as an exciton in a quantum dot or an impurity state (NV center) in a diamond, and control its wavefunction – that is to say, prepare it in a specified state. While this can be done by exciting with suitable tuned laser pulses, the process is limited by the interaction with the phonons (lattice vibrations) in the surrounding crystal. The aim of this project is to predict theoretically (by solving a master equation for the density operator) the change in the phonon occupations caused by the state control process. This would allow us to propose a design for a refrigerator using the simplest possible quantum object – a single two-level system – as a working medium, and opens up interesting issues relating to thermodynamics at the nanoscale.

**Section 1 – Supervisor Details**

**Name:** Dr Brian Espey

**School:** Physics

**Email:** Brian.Espey@tcd.ie

**Section 2 – Project Details**

**Project Title:** Tomography of light pollution

**Project Description (500 words or less):**

Outline:
Measurements of light pollution are in their infancy in Ireland. This project aims to advance our knowledge of light pollution after the Celtic Tiger building boom by using a combination of ground-based measurements and satellite and International Space Station data to determine the sources and strengths of light pollution. The project will involve a computer-based approach to analyse using available astronomy packages, although it will also be possible to implement scripting to automate some of these.

Dataset: Ground-based data includes fisheye digital camera images which will be calibrated in terms of orientation and pixel intensity for intercomparison with images from other sites. The goal of this work is to triangulate the "light domes" due to intense light sources, and to determine their nature (e.g., whether due to street lighting, commercial floodlighting, or private dwellings).

Purpose: The recent award of Dark Sky Reserve status by the International Dark Sky Association to the Kerry Dark Sky Reserve provides an indication of the quality of skies available in Ireland, and there is a significant tourism – as well as environmental – element to this work. The

development of the tools in this project will aid in protecting this, and other, areas by enabling the number, type, and nature of intrusive light sources to be identified so that action can be taken to ameliorate the problem. The calibrated data will also serve as a resource to be added to a database of light conditions across the country, and a report will be generated that can lead to a publication.

Technique: Data are obtained from all-sky images taken with fish-eye lens adapters and recorded in raw digital format on a Digital SLR. Stars identified in the field provide a means of calibrating the recorded intensity in Analog-to-Digital Units (ADUs, or "counts"). Based on this calibration the whole image can be processed to provide quantitative intensities of the sky background on a pixel-by-pixel basis, and also the intensities of nearby sources of light. Knowing the time of the exposure, and the starfield, orientation can be calibrated, permitting the azimuth of any light sources to be determined; when combined with information from other sites, this permits the locations of light sources to be determined. Additional information comes from the colour intensities contained in each of the RGB filtered images that make up the raw data image – these provide an indication of the nature and amount of light from each light source (e.g., white light, low pressure sodium, high pressure sodium). These results can be correlated against the location and intensities obtained from satellite data such as the SUOMI/VIIRS instrument, or the data taken by astronauts from the International Space Station (ISS).

Pre-requisites: Computer experience, preferably with coding/data analysis skills.

Section 1 – Supervisor Details

**Name:** Dr Peter T. Gallagher

**School:** Physics

**Email:** peter.gallagher@tcd.ie

**Section 2 – Project Details**

**Project Title: Software Development for www.SolarMonitor.org**

**Project Description (500 words or less):** The TCD Solar Physics Group runs a popular website called www.SolarMonitor.org that serves near-realtime images of the Sun from a number of NASA, NOAA and ESA satellites to over 3,500 visitors each day. We require a summer intern to work on the backend software to improve the stability and functionality of the website. The intern will work closely with members of the group on IDL code to process and archive data from a multitude of solar and space weather databases around the world. Experience with Interactive Data Language (IDL) desirable.

## Section 1 – Supervisor Details

**Name:** Professor Stefan Hutzler

**School:** Physics

**Email:** stefan.hutzler@tcd.ie

## Section 2 – Project Details

**Project Title:** Experimenting with foams

**Project Description (500 words or less):**

Foams are all around us. They can be seen at the sea shore after a storm, at the top of a pint of beer, or when we wash our hair. To a physicist they pose a variety of questions. What are the shapes of the bubbles? How are they packed? How does liquid flow through a foam? How does foam flow when sheared?

Fundamental in nature, these questions are also of great importance for many industrial applications. The mechanical properties of foam as a material is of relevance for example to foamed metals, that have been produced by bubbling gas through a melt. Companies producing private care products are interested in characterising the foamabilitiy of

shampoos.

In this project the summer student will carry out a number of exploratory studies in foam physics, concerning foam drainage, equilibrium configurations of foam films in the presence of fibres, and bubble-bubble interaction.

Reference: Weaire D and Hutzler S, The physics of foams, Clarendon Press, Oxford, 1999.

## Section 1 – Supervisor Details

**Name:** Prof. Matthias Möbius (in collaboration with Prof. J.M.D. Coey)

**School:** Physics

**Email:** mobiusm@tcd.ie

## Section 2 – Project Details

## Project Title: Bubble formation at gas-evolving micro electrodes

## Project Description:

The stability of nanobubbles in water is an enduring mystery; they should dissolve in a trice due to the Laplace pressure. Microbubbles which are widely used in microfluidic devices, for drug delivery and as ultrasonic contrast agents are better understood [1], but size control and uniformity remain a challenge because of hydrodynamic instability during bubble formation [2,3]. Here, we will create hydrogen bubbles on a micro- or nano-electrode by electrolysis in a controlled way in order to study the effect of surface tension on bubble coalescence [4] and the magnetohydrodynamics of the process.

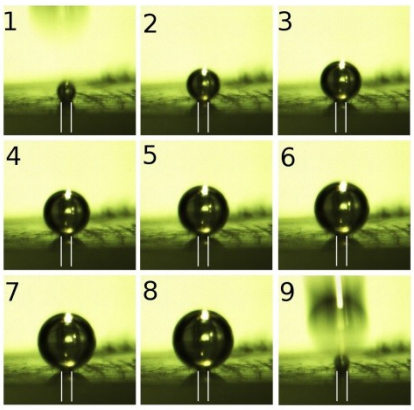



Figure 1: Time evolution of a bubble growing on a Platinum micro-electrode.

The student will investigate the influence of surface tension and ion species on bubble formation during electrolysis. Electrodes will be patterned by UV or e-beam lithography. High speed video imaging will help elucidate the hydrodynamics. Experiments will be coupled with computer simulations and analytical theory to address a puzzling problem. Some knowledge of hydrodynamics and image processing would be beneficial.

**References**

**[1]** J.R. Lindner, Nature Reviews 3, 527 (2004)
**[2]** E. Stride, M. Edirisinghe, Med. Biol. Eng. Comput., (2009)
**[3]** B. Dollet et al., PRL 100, 034504 (2008);
**[4]** D. Fernández, P. Maurer, M. Martine, J.M.D. Coey and M. Möbius (in review).

**Section 1 – Supervisor Details**

**Name:** Dr David D. O'Regan

**School:** Physics

**Email:** david.o.regan@tcd.ie

**Section 2 – Project Details**

**Project Title:** Quantum-mechanical simulation of magneto-optical spectroscopy in chiral nanotubes and DNA

**Project Description (500 words or less):**

Certain materials exhibit the phenomenon of rotating linearly-polarised light passing through them, an effect known as optical activity or magneto-optical response. The related spectroscopic techniques, in particular, electronic circular dichroism (ECD) and optical rotatory dispersion (ORD) directly probe the chirality of the material in question. These techniques are particularly important for characterising similar molecules or nanostructures with different chirality, whose absorption spectra may be identical but whose magneto-optical may differ enormously. ECD also plays a role in the study of magnetic materials with a strong orbital component to magnetism.

Experimental ECD signals are often very clear, but can be difficult to understand without some prior knowledge of the crystal structure. This is why a theoretical description, necessarily quantum-mechanical, is an essential, but hitherto almost entirely absent, companion to experimental magneto-optical spectroscopy. Up to now, relatively very few first-principles quantum calculations of magneto-optical spectra have been carried out, and code for carrying them out is not very widely available.

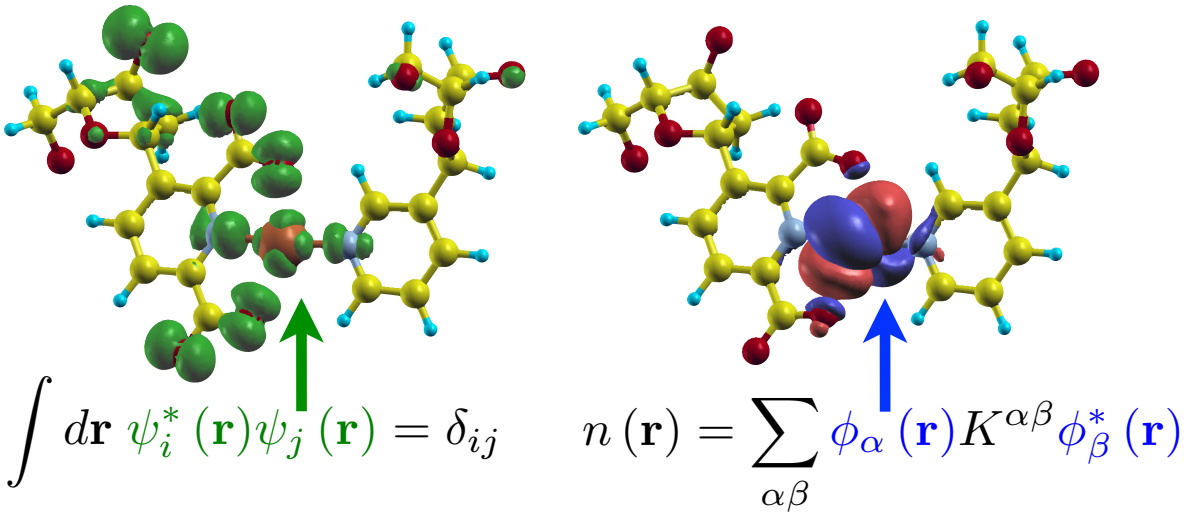



Figure: ONETEP simulation of a modified, copper-intercalating DNA base-pair, with (left) a delocalised single-particle state, and (right) a localised Wannier orbital used to exploit the quantum "near-sighted" property.

The proposed project first entails a study of the rather interesting quantum-mechanical theory of angular momentum and related magneto-optical response, and how they can be computed using the output of computer simulations using a very successful (Nobel winning) [1] and widely used atomistic simulation method known as density-functional theory (DFT), and its linear-scaling generalisation.

We will then implement (in parallelised code and in relatively self-contained modifications to the linear-scaling DFT package ONETEP [2-5] an experimentally-relevant model for ECD and ORD. Some very interesting theory and technical points must be addressed in order to produce a practical implementation, such as the open issue of gauge invariance with finite basis-sets [6,7]. The dynamical extension of DFT to time-dependent DFT will also be considered [8].

In ONETEP, certain locality properties of quantum systems are exploited to ensure a linear-scaling increase in computational cost with increasing system size, where conventional DFT codes scale cubically and are limited, at present, to a few hundred atoms. This is necessary to ensure that we can compute spectra for reasonably large systems, and we will test to make sure that our implementation of ECD and ORD preserves linear-scaling, in which case it would be the first such implementation of its kind.

Finally, we will compute ECD and ORD spectra for some chiral molecules and nanostructures of cutting-edge importance, in particular DNA base-pairs, guanine quadruplex (four-stranded) DNA [9], and chiral nanotubes [10], which have never been computed before now to our knowledge. We will make direct comparison to experimental spectra, and investigate any discrepancy between theory and experiment.

[1] http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1998/press.html

[2] www.onetep.org

[3] C.-K. Skylaris et al., J. Chem. Phys. 122, 084119 (2005).

[4] M. Heiss et al., Nature Materials 12, 439–444 (2013).

[5] L. E. Ratcliff et al., Phys. Rev. B. 84, 165131 (2011).

[6] D. Varsano et al., Phys. Chem. Chem. Phys., 2009, 11, 4481.

[7] K.-M. Lee et al., J. Chem. Phys. 134, 144106 (2011).

[8] T. J. Zuehlsdorff et al., J. Chem. Phys. 139, 064104 (2013).

[9] D. Sen and W. Gilbert, Nature 334, 364 (1988).

[10] S. Iijima, Nature 354, 56 (1991).

## Section 1 – Supervisor Details

**Name:** Dr Ramesh Babu

**School: School of** Physics and CRANN

**Email:** babup@tcd.ie

**Website:** http://physics.tcd.ie/pmnc/

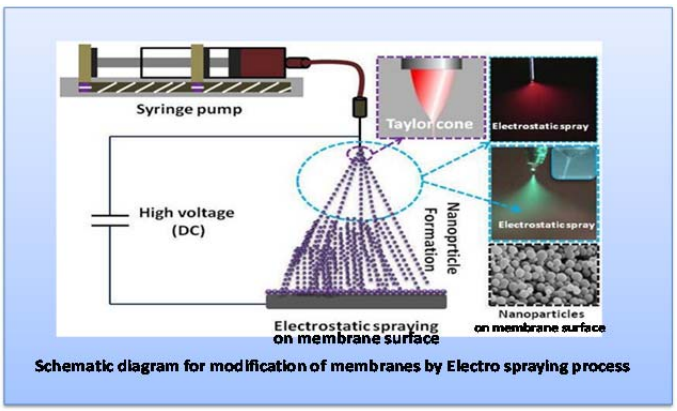
## Section 2 – Project Details

**Project Title:** **Functionalization of membrane surfaces by Electro spinning and Spraying**

**Project Description (500 words or less):** Membrane based technologies is in the state of rapid growth and widely accepted as an integral part of various industrial sectors and especially in producing the clean water, energy, pharmaceuticals, functional foods and many more areas. The advantage of membrane based separation processes is simplicity in concept and operation, not involving any phase changes or chemical additives, being modular and easy to scale up and low energy consumption. All these advantages translate into cost savings and more environmentally sustainable process. Despite such significant advantages, conventional polymeric membranes suffer from various shortcomings including low-flux and high fouling tendency and often require functionalization or replacing the membrane with different polymeric membrane in order to make the separation process cost-effective.

Electro spraying is a versatile processing technique which produces ultrafine nano fibres or particles with an electrical driving force. The diverse real-world applications of this process have continued to steadily grow over recent years and include such areas as high performance air filters, sensors, textiles, medical wound dressing, photovoltaic cells, fuel cells, batteries, capacitors, and scaffolds for tissue engineering (1). The main advantages of this technique are easy to setup, high speed, low cost of the process for the mass-scale fabrication of one-dimensional and anisotropic nano materials than other conventional fabrication techniques such as chemical vapour deposition, lithography, hydrothermal, etc. and can be used deposit various high surface nanoparticles/fibres to functionalise the surface of the membranes for improve separation performance.

The aim of this project is to understand the process of electro spraying and modifying the commercial ultra and micro filtration membranes using selected hydrophilic polymers and nano fillers. The modified membranes will be evaluated for separation of proteins and filtration of waste water streams form dairy industry. In addition, the project will also provide the student with a background understanding of various nano-additives for surface modification of polymers in general. The student will receive instruction in good laboratory practice, work in a challenging high skills environment with experienced researchers, develop his/her knowledge of polymeric membranes and gain exposure to various instruments used to characterize these polymers and membranes.




Schematic diagram for modification of membranes by Electro spraying process

**References**

[1] 1. James J. Doyle, Santosh Choudhari, Seeram Ramakrishna, and Ramesh P. Babu, *Conference Papers in Materials Science*, vol. 2013, Article ID 269313, 1-14.

[2] Zuwei Ma, Seeram Ramakrishna *Journal of Membrane Science* 319 (2008) 23–28

[3] R.S. Barhate, Seeram Ramakrishna *Journal of Membrane Science* 296 (2007) 1–8.

## Section 1 – Supervisor Details

**Name:** Dr C. S. Clotilde; Prof. S. Sanvito

**School:** Physics

**Email:** c.cucinotta@tcd.ie; sanvitos@tcd.ie

## Section 2 – Project Details

**Project Title:** Toward a realistic model of oxidation processes occurring at the anodic chamber of solid oxide fuel cells.

**Project Description:**

The problem:
Irish energy policy prioritizes the development of renewable energy technologies and energy efficiency in order to meet 2020 commitments. The further optimization of electrochemical devices such as solid oxide fuel cells (SOFCs) enables a more efficient and sustainable energy utilization.
In SOFCs a Hydrogen rich fuel reacts with the oxidizing agent $O_2$. Fuel and oxygen are supplied at the opposite sides of a ceramic thin film electrolyte - typically yttria stabilized zirconia (YSZ)- through which $O^{2-}$ ions diffuse to combine at the opposite side with $H^+$, at the triple phase boundary (TPB) region, i.e. at the interface between the anode, the electrolyte and the gas phase. This produces electrons, i.e. electric power (see Figure 1).

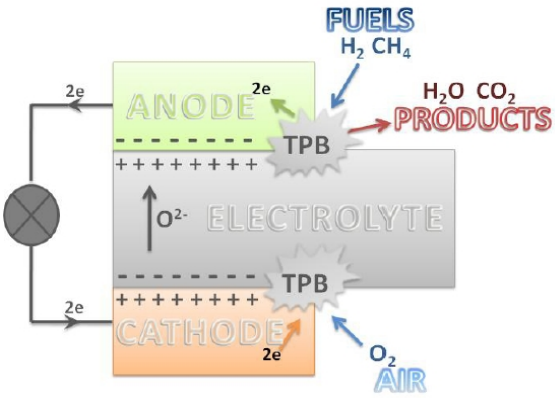



Figure 1: Operation of a solid oxide fuel cell.

SOFCs find a natural application as Combined Heat and Power (CHP) devices. In CHP electricity is

generated on site, avoiding transmission losses. his can lead to 35 per cent reduction in primary energy usage - compared to conventional power stations and methane fueled boilers - corresponding in Ireland to economic savings of 800 € per household, only in the residential sector.

A deeper understanding of the elementary steps in fuel oxidation than currently exists is mandatory to go beyond a mere trial and error procedure in the design of new materials and geometries for SOFC, however, the detailed microscopic mechanism of fuel oxidation at the anode is still matter for debate. Not only it is unclear whether the formation of $H_2O$ takes place on the metal or at the electrolyte surface, but also the precise composition of the region in the vicinity of the double layer is basically unknown.

*Aim:* During this summership a realistic model of the anode / YSZ interface in SOFCs will be developed and *the thermodynamics of key fuel oxidation process* $[2H_2+O^{2-} \Rightarrow H_2O +2e^-]$ studied.

*Central research questions:*
*- What is the best model for the electrode/electrolyte interface (metal oxide or interfacial oxide)?*
*- What is the role of nano-structuring in the efficiency of a SOFC?*

*Models and methods:*
*A suitable model for the anode/YSZ interface is essential. The structural and transport properties of the TPB depend on its composition and deeply affect the performance of a fuel cell.*

*Experiments have shown the* occurrence of anode oxidation. Previous computational studies [Cucinotta2011] evidenced *the crucial role in the oxidation process of the presence of additional O atoms at the interface with the anode.*

During this summership the idea that fuel oxidation is mediated by a NiO interlayer will be addressed, developing a realistic model for the TPB, represented by a Ni/NiO/YSZ nanostructure.

Using the parameter free Density Functional Theory approach, different configurations for the electrode-oxide-electrolyte interface will be compared and the role of point defects in its formation studied.
*The Thermodynamics of key oxidation steps will be compared with that in a standard Ni/YSZ cermet.*

[Cucinotta2011]: C. S. Cucinotta, M. Bernasconi,. and M. Parrinello, Phys. Rev. Lett. 107, 206103 (2011).

## Section 1 – Supervisor Details

**Name:** Dr Thomas Archer

**School:** Physics

**Email:** archert@tcd.ie

## Section 2 – Project Details

## Project Title: Predicting new magnetic materials

## Project Description (500 words or less):

Permanent magnets are now commodities in many industrial sectors, ranging from data storage to clean energy. For instance a top capacity wind turbine currently requires about 2 tons of high-performance permanent magnets. At present such permanent magnets have a high content of critical elements, namely rare-earths and platinum group metals. These are both expensive and, due to a combination of geopolitical reasons, volatile in price. This volatility hampers the uptake of new technology. We are aiming to find new magnetic materials to replace rare earth magnets.

Modern quantum mechanical modelling techniques are capable of accurately describing the properties of materials; coupled with the vast amount of computational power now available, has led to the new concept of materials designed namely “high-throughput computing”. We have created a database containing calculations of 250,000 potentially new materials, to put this in context the number of materials currently known to science is 50,000. The database has already been used to predict 23 new magnetic materials, however there is much more potential.

This project is to develop data-mining techniques to search for patterns in the calculated database. These patterns will be used to gain physical insight and to select most promising candidates to add to the database.

## Section 1 – Supervisor Details

**Name:** Prof. Stefano Sanvito

**School:** Physics

**Email:** sanvitos@tcd.ie

## Section 2 – Project Details

**Project Title:** Tetragonal distorted Heusler alloys

## Project Description (500 words or less):

Heusler alloys are a vast class of materials displaying a multitude of interesting electronic structures. These are ternary materials (the formula unit is $A_2BC$, e.g. $Ni_2MnGa$) with electronic properties ranging from magnetism, to superconductivity, to topological phases, to thermoelectricity. An interesting sub-class of the Heusler family is that of the tetragonal distorted compounds. These are often magnetic and the distortion usually brings a significant magnetic anisotropy. Interestingly, the occurrence of the distortion seems to be a rather rare event within this class of materials, with only 14 known compounds over the several hundreds known Heuslers displaying the distortion. Most importantly the tetragonal distortion does not seem to correlate with the chemical composition of the specific Heusler and its microscopic origin is not clear at present.

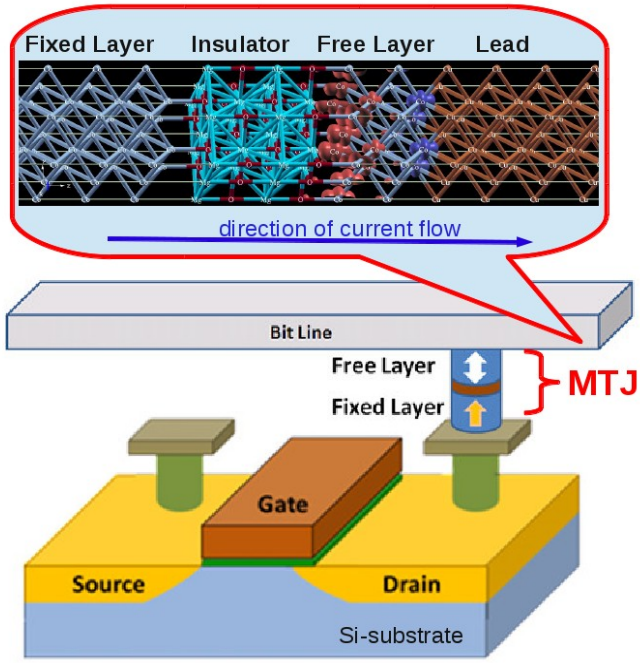
In this project the student will perform numerical simulations for a range of Heusler compounds in the search for the possible mechanism for the tetragonal distortion. The main theoretical tool will be Density Functional Theory, today the most accurate and versatile methods for ground state electronic structure. The calculations will be rationalized with the use of an empirical free energy, which will help us in describing the phase diagram of this interesting class of materials.

## Section 1 – Supervisor Details

**Name:** Dr Stefano Sanvito

**School:** Physics

**Email:** sanvitos@tcd.ie



STT-MRAM cell

## Section 2 – Project Details

### Simulating the switching of a memory cell in STT-MRAM

### Project Description:

Currently there is a worldwide effort towards developing high-density, cheap and fast memory solutions to sustain our ever-growing demand for storing data. In particular, crucial is the development of new random-access memories (RAMs). Together with the need for further increase in read/write speed and a reduction of size and energy consumption, the future RAMs should also be non-volatile, so that they are able to preserve information without a constant power supply. From about ten different candidate technologies listed in the International Technology Roadmap for Semiconductors (ITRS) over the past few years, one is especially promising and largely accepted by microelectronics industry as the most likely solution for the next generation RAM. This is the so-called spin transfer torque magnetic RAM (STT-MRAM).

The STT-MRAM uses the magnetic state of a nano-scopic device, the magnetic tunnel junction (MTJ), to store one bit of information and that state is read or written by electrical currents flowing through the MTJ (see the figure). Each MTJ is a thin-film stack with two key magnetic layers, one hard (not free to rotate) and one soft (free to rotate), separated by an insulator. The MTJ's electrical resistance depends on the mutual orientation of the magnetisation of the layers (*tunneling magneto-resistance* – TMR – effect), which constitutes the information stored in the STT-MRAM cell. Electrical current through the MTJ is spin-polarized by the fixed layer and exchanges angular momentum with the free layer, hence generating a spin transfer torque (STT), which drives magnetisation reversal of the

free layer. It is therefore possible to change the information stored in a specific cell by applying a current pulse. In the strive for the optimal STT-MRAM cell composition, together with the actual laboratory work on fabrication, theory can have a significant input and some of the industrial partners in CRANN have already expressed their strong interest in the theoretical developments in this field.
While the basic principles are established, the actual microscopic mechanisms governing the switching process and their sensitivity to particular material or atomistic detail, are not yet fully understood. This project will involve numerical simulations of the switching process of an MTJ within a MRAM cell. The aim is to determine the key aspects that govern the switching process. The student will use established software packages for micro-magnetic simulations that will allow him/her to study the dynamics of a current-induced free layer magnetisation reversal in realistic MTJ systems. A novel element to the existing micro-magnetic solver will be inclusion of parameters obtained from quantum transport calculations for the material and structure specific torque efficiency. This will allow the students to predict the switching properties of novel junction stacks, where no experimental data is available.

# Nanosized Clusters and Bio-Inorganic Network Structures for Sustainable Energy Applications

## Section 1 – Supervisor Details

**Name: Dr. Wolfgang Schmitt**

**School: School of Chemistry**

**Position: Lecturer in Inorganic and Materials Chemistry**

**Email: schmittw@tcd.ie**

**Project Description:** Organic-inorganic coordination networks and cluster compounds represent classes of supramolecular compounds whose preparation is a very active area in chemical and materials research. The concept of hybrid organic-inorganic materials presents a means to customize physical and chemical properties by reducing the dimensionality of classical inorganic materials within organic matrices. This approach allows a combination of the advantageous properties of inorganic and organic materials. **Our research aims to design and exploit these materials for sustainable energy applications. We are interested in hydrogen storage and bio-inorganic approaches to capture and activate $CO_2$ to produce industrially important chemicals.**

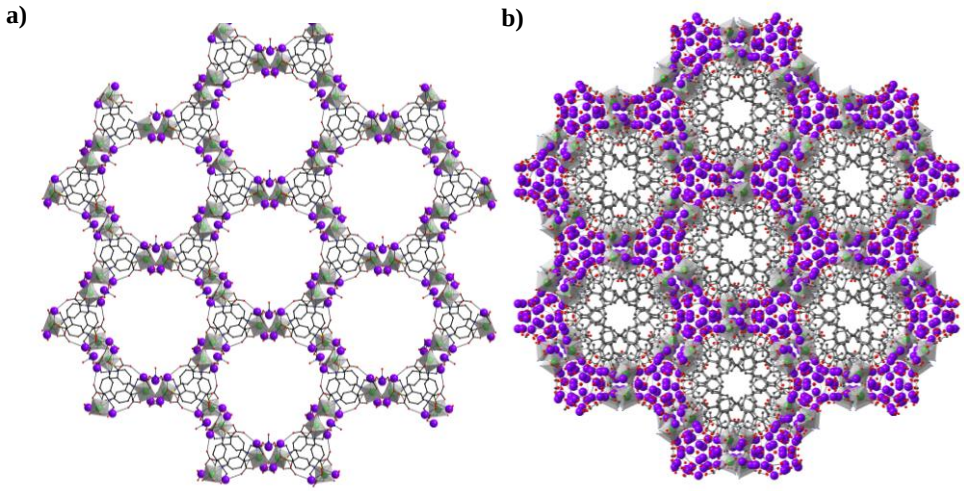



**Figure 1:** Open frameworks for hydrogen storage: a) Open-framework with chiral channels, $K_6[Fe_2(\mu\text{-}O)(\mu\text{-}CO_3)L_2]$. b) Dense honeycomb-structure $K_6[Fe_2(\mu\text{-}O)(\mu\text{-}CO_3)]$. Fe green, O red, K purple, C grey.

**$H_2$-Storage Materials:** Hydrogen energy systems are expected to revolutionize the way economies are powered, offering cleaner, efficient, politically independent alternatives to the combustion of fossil fuels. Developing safe hydrogen storage technologies that fulfil performance and cost requirements is critical to achieving a hydrogen economy. Recently, many industrial countries have reinforced their research to exploit the properties of organic-inorganic networks to shift from oil towards a sustainable hydrogen economy as these materials have potentially excellent $H_2$ storage capabilities. One focus of our research activities addresses the question of how 3D architectures of organic-inorganic frameworks (see Fig.1) can be rationally optimized to possess excellent $H_2$ storage capabilities.

**Bio-Inorganic Activation of $CO_2$:** $CO_2$ is a greenhouse gas and its significant role on global warming is undeniable. However $CO_2$ is also a life sustaining compound. It is used by plants in photosynthesis processes to produce sugars which are energy source and raw materials for starch and cellulose, proteins and a variety of other organic compounds. High prices and a limited availability of fossil fuels provide motivation for scientists to replicate the photosynthesis and the $CO_2$ activation in 'test tubes'. However, $CO_2$ is inert and very stable and its conversion into useful compounds is highly challenging. We are developing metal clusters (Fig. 2) that replicate functionalities of biological enzymes. The clusters operate in aqueous systems and display a high affinity to capture $CO_2$. Inspired by nature we aim to use light irradiation to photo-reduce the activated $CO_2$ in order to produce alcohols and aldehyds.

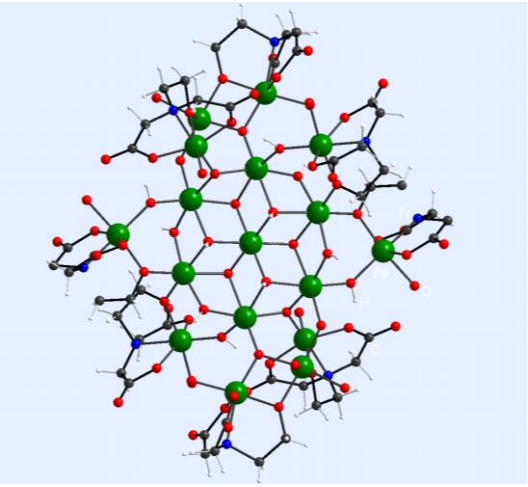


**Figure 2:** Nano-sized $Fe^{III}$-oxo cluster (containing 17 Fe atoms) that will be used for the fixation and activation of atmospheric $CO_2$. Colour Code: Fe green, O red, N blue, C grey

**Methodology & Project:** We have developed synthetic concepts for unique open-framework structures and cluster compounds. To prepare the network structures for $H_2$ storage applications we investigate the structure-directing effects of substituted organic phenols and naphthols. These ligands (L) react with $Fe^{III}$ salts to dinuclear $[Fe_2(\mu\text{-}O)(\mu\text{-}CO_3)L_2]^{4-/6-}$ complexes that assemble in the presence of positively charged counterions (e.g. potassium ions) into cross-linked network structures (Fig. 1). If the organic ligand structure is modified, the reaction with $Fe^{III}$ salts results in cluster compounds (single molecules and not networks) which are able to fix and activate atmospheric $CO_2$ (Fig. 2). We investigate how light irradiation initiates the reduction of $CO_2$ to produce methanol. The SURE student will synthesise new organic ligands and react these with transition metals to produce novel coordination networks and cluster compounds. The molecular structures of these compounds will be investigated by single crystal X-ray diffraction. Further instrumental analyses include thermogravimetric studies, UV-VIS infrared-spectroscopy and BET surface area analysis. The student will explore the reactivity of the cluster compounds and will investigate photo-reductions to activate $CO_2$.

See: http://www.tcd.ie/Chemistry/staff/people/Schmitt/index.html

## Section 1 – Supervisor Details

**Name:** Professor Igor Shvets

**School:** Physics

**Email:** ivchvets@tcd.ie

## Section 2 – Project Details

**Project Title**: **Atomic Force Microscopy Investigations of Vicinal Substrates**

## Project Description

A novel technique for the fabrication of material independent planar arrays of nanoparticle has been developed by the Applied Physics Research Group, Trinity College Dublin. The technique is entitled Atomic Terrace Low Angle Shadowing (ATLAS). The technique involves a low incident angle flux of material onto a vicinal (mis-cut) substrate. A vicinal substrate comprises of atomic terraces separated by atomic steps. The best analogy is to think of a vicinal substrate as a staircase structure. Due to the low angle of incidence of the flux material, the atomic steps shadow some of the area of each atomic terrace. In this manner material can only be deposited on either the inner or outer portion of each atomic step, depending on the direction of the flux material. For the successful operation of the ATLAS technique we require control over the vicinal surface morphology. The rationale is the vicinal substrate morphology dictates the separation and density of the planar nanoparticle arrays.

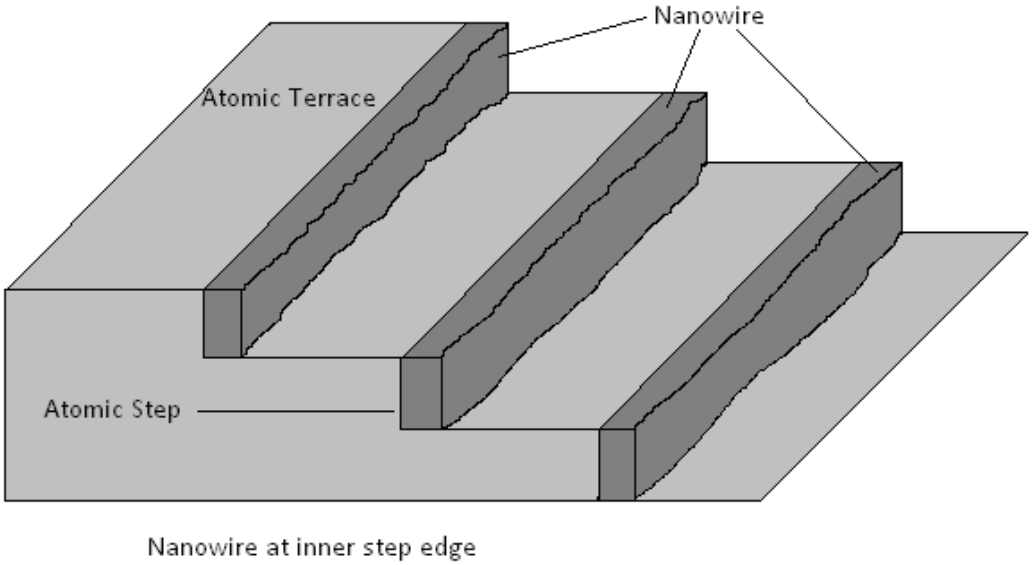



**Figure 1:** Schematic of nanoparticles formed at the inner step edges of a vicinal substrate

We have developed several regimes to control the vicinal surface morphology through a process of step-bunching. Step-bunching involves the controlled forcing of separate atomic steps to come together to form bigger steps. The height of the new step and its separation from the other steps is dictated by how many steps join to form the new step. We can force the steps to bunch through a process of thermal annealing (heating the substrate at high temperatures for long periods of time) or by applying a current along the surface at a constant temperature, a process called electromigration.

We have devised a method to investigate the influence of electromigration on step bunching on vicinal substrates. Central to this was the development of a new heating element which allows us to separate the applied current and the temperature, thus allowing us to pass a current of variable size through a sample at a constant temperature. The applied current causes the surface adatoms to drift as a result of the electromigration force acting on them. The size of the force if given by: $F = q_{eff}E$, where $q_{eff}$ is the adatom effective charge and $E$ is the applied electric field. A schematic of the heater is shown below, Figure 2.

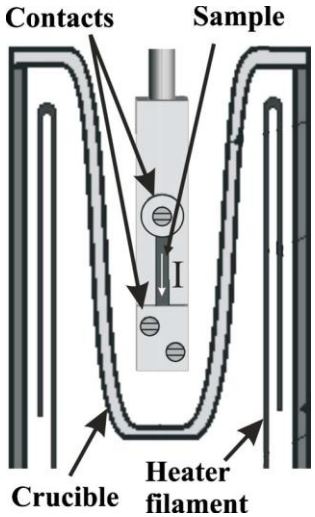



**Figure 2:** Schematic of heater that allows for the passage of an electric current at constant temperature.

To further our knowledge of the electromigration effect on step bunching we have to perform rigorous testing of many temperature regimes and electric current values. The project will comprise the following tasks:

1. Electromigration studies for a range of applied current at a range of constant temperatures
2. Atomic Force Microscopy (AFM) investigations of the resulting step-bunching

Task 1: Involves the formation of step-bunching samples using a range of applied current values at constant temperatures. The experimental set-up available in the Applied Physics Research Group will be used for this task, including the heater shown in Figure 2, above.

Task 2: Involves the analysis of the step-bunched samples generated in Task 1 via Atomic Force Microscopy (AFM). For this the ambient AFM instrument available in the Applied Physics Research Group will be used. If necessary we will use more advanced imaging techniques available through the Advanced Microscopy Laboratory located in the Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN).

## Section 1 – Supervisor Details

**Name:** Dr Hongzhou Zhang

**School:** Physics

**Email:** hozhang@tcd.ie

## Section 2 – Project Details

### The development of cathodoluminescence detection in the Scanning Electron microscope

Catholoumminescence (CL) is the process of light emission due to energetic electron bombardment and it is a conventional analytical method material characterisation. We have recently integrated a novel fibre based CL detection system with a scanning electron microscopy. The task of this project is to further improve the detection efficiency and design practical approaches for quantification of detection geometry.

The candidate is expected to finish a literature review on the approaches for the fibre tip modification and conduct experiments to modify the fibre using mechanical polishing as well as heat treatment to improve the detection efficiency. It is also possible to work on the focused ion beam workstation to fabricate photonic structures on the tip.

Hands-on trainings on the operation of the scanning electron microscope, nanomanipulator, and spectrometer will be available to the student. The student will be actively involved in relevant research activities in the group and hopefully make contributions to the characterisation of nanosensors using the improved CL setup.