

**EPSRC Centre for Doctoral Training
in the Advanced Characterisation of Materials**

**Project List and Outlines 2017/18**

1. **Characterisation of catalytic nanoparticles and their interactions with biological fluids for diagnostics**The development of nanoparticle sensing components that can perform catalytic reactions but avoid surface fouling following contact with biological liquids such as plasma serum or cerebrospinal fluid is of profound interest for biosensing applications. Using the highest end available techniques this PhD aims to characterise the growth and surface modification of catalytic nanoparticles in various conditions and explore the way certain particles are able to retain catalytic activity despite being exposed to proteins and other biological molecules and to extend this knowledge to the development of new and advance components for sensing technologies.
2. **Optimising solar hydrogen production through studies of ultrafast dynamics**TiO2 remains the subject of intense research associated with its photocatalytic properties. Indeed, understanding how the TiO2/water system works at the level of individual atoms and molecules is one of the grand challenges of contemporary physical science. In this project we will focus on the dynamics, in particular that associated with plasmonic enhancement by gold nanoparticles. This will be studied in tandem with ultrafast interfacial energy-transfer processes associated with model photocatalysis and solar energy conversion involving TiO2. Although models to describe the associated phenomenon have been in place for many years, there have been no direct measurements of the electron state dynamics to test these ideas. This work has the potential to provide a major breakthrough in our understanding of the mechanisms involved and hence suggest ways of improving the efficiency of TiO2 and related light harvesting systems.
3. **The Ultra-Structure of the Bone Interface Adjacent to Different Bone Graft Substitute Materials**The aims of this project are to describe the ultrastructure of the bone implant interface adjacent to bone graft substitute (BGS) materials with different compositions. The objective of the project would be to describe the structure of the interface and relate this to the bioactivity of the bone graft substitute. Description of the project: A number of bone graft substitute material are commercially used. These materials vary in their structure and in resorption rate but are all contain calcium phosphate. There is evidence to suggest that different compositions induce different types of bone formation. For example some are able to elicit bone formation in a soft tissue site (osteoinduction), whereas other BGS are unable to do this 1. Some BGS induce endochondral ossification whilst others induce intramembranous ossification.
4. **Laser damage pathways in nanocrystalline materials**In anticipation of new ultrafast X-ray sources for materials characterisation, such as XFELs, this project aims to carry out materials investigations of pre-damaged materials. We will expose a range of single-crystal and polycrystalline samples to controlled doses of focussed ultrafast laser pulses, sufficient to ablate some of the material and/or cause highly localized ionization and heating. The patterns of strain produced within individual crystal grains in the immediate vicinity of the resulting crater/damage site will be probed by Bragg Coherent X-ray Diffraction Imaging (BCDI). These will be compared with current thermal and electronic models of the ultrafast processing of the material. Metallic and dielectric samples are expected to give interesting results. The project should lead naturally to future pump-probe investigations of damage pathways in which a powerful laser is used to generate and excited state of matter which is probed femtoseconds to microseconds later with a short-pulse X-ray beam. The combinations of facilities needed to achieve this are scarce, but more are under construction.
5. **Gold Nanoparticles- from Plasmonics to Stopping Hospital Acquired Infections**The aim of the project is to make gold nanoparticles with very controlled sizes and shapes to induce optimised plasmonic effects that will be used for various applications including optical processing and as catalysts to create antimicrobial surfaces. The key aim will be to create surfaces that could be used to reduce the incidence of hospital acquired infection.Hospital acquired infections (HAI) cost the NHS more than £1B and cause more than 5,000 deaths per year. All admitted patients have a 10% chance of contracting an HAI. This risk is increased further for catheterised patient to a 10% additive chance per day whilst the catheter is in place. Some of these infections are due to superbugs- particularly MRSA, E-Coli and C.Diff. that are resistant to antibiotics. A new strategy developed at UCL is to create coatings that self-sterilise- and eliminate bacteria [1-3]. We have found that coupling gold nanoparticles with a range of light- activated dyes, such as crystal violet, creates surfaces that kill bacteria both in the lab and through clinical trials in hospitals. At present we have an incomplete knowledge of how these coatings work and why the use of gold nanoparticles give up to a million-fold enhancement in the bacteria kill. Imperial college have extensive experience in studying the optical effects of gold nanoparticles and have used this to generate photonic enhancements and coupled plasmonic devices. The project needs both UCL and IC as neither university has the skill set to do the project in isolation. UCL is skilled in antimicrobial testing, nanoparticle synthesis and hospital trials. IC brings the necessary skills in optical-modelling, laser based measurements, and photonics. A combination of both universities skills will enable us to understand the underpinning science of why gold nanoparticles give such an enhancement in bacteria kills and enable us to optimise the potency of the new surfaces. In the last year of the project it is envisaged that we will have prepared optimised materials and started clinical trials at both UCLH and IC Hammersmith hospitals.
6. **Spin-selective transport in chiral organic semiconducting materials**Chirality is a fundamental symmetry property. Objects are defined as chiral if they exist as a pair of “left handed” or “right handed” mirror images that cannot be superimposed. Most conjugated organic semiconducting materials used in organic electronic devices are non-chiral. Chiral organic materials are being increasingly recognised as useful for future applications however, where such applications are dependent on the chirality of the material. Key examples include the use of chiral materials in spintronic applications,1 as chiral sensors,2 and in circularly polarized (CP)-photodiodes3 and OLEDs.4 Fuchter and Campbell have recently reported that the first CP-light detecting photo-FETs (see insert)5 can be fabricated from chiral organic small molecules; devices which can detect and differentiate left and right handed CP irradiation. There are many questions remaining over how the chirality of the organic semiconductor in such applications effects charge transport and, in turn, device function. It has been reported that charge conduction through chiral materials is spin selective6 and therefore spin dependent effects are likely a highly important but not currently well-understood phenomenon in such contexts. The aim of this project is to address this gap in our fundamental understanding of spin-selective charge transport in chiral organic materials.
7. **Nanoscale Engineering of Multifunctional Probes for Cancer Diagnosis and Therapeutics**The cancer survival rate decreases exponentially in late stage diagnosis. Unfortunately, early detection for cancer remains a major unmet clinical need. Imaging has become an indispensable tool in early cancer diagnosis and surgical guidance. Fluorescence-based optical imaging has the advantage of fast feedback as well as high spatial resolution, compared to tomographic imaging techniques. In this project, we aim to design and develop a novel strategy to functionalise ‘carriers’ with multiple groups in order to diagnosis cancer at early stage as well as deliver drugs to the specific cancerous sites for treatment. Plasmonic nanostructures such as Au nanorods will be served as ‘carriers’ for cancer diagnosis and therapeutics. The nanoparticles will be functionalized with fluorescent dyes for imaging, tumour specific ligand for cancer cell targeting, and anti-cancer drug loading for therapeutics. The designed ‘carriers’ will then be tested in cell lines to conduct biocompability and toxicity studies.

The proposed research will provide a paradigm shift in cancer diagnosis and treatment, by employing the novel functionalized ‘carrier’ platform. The translational work will be further investigated in animal models and we expect it will enhance the clinical opportunity for treatment of cancer and has the potential to significantly improve survival rates, reducing mortality and morbidity and therefore resulting in improved quality of life and lower cost of care. This is an excellent example of how nanotechnology can find an application in healthcare to improve human wellbeing.

1. **Nanomechanical characterisation of soft materials**The project objective is to develop a suite of analytical techniques, including optical tweezers and microfluidics, for characterising the (nano)mechanical properties of ‘soft’ materials such as liposomes or biomembranes. The principal aims of this project are:
(i) to study the mechanical properties of biomimetic vesicles undergoing extreme deformations as a result of an applied external stress, e.g. optical, acoustic, or fluid shear forces;
(ii) to study phase separation and rupture in artificial vesicles under external forcing;
(iii) to use the result of the above studies to engineer membrane materials with properties optimised for applications including controlled drug release and microreactors.
During the project the student will acquire skills in microfluidics, microdevice fabrication, optics, modelling (including light scattering and transport phenomena), image analysis, and (micro)rheology.
2. **Determining the structure and mechanism of anti-bacterial ZnO nanoparticle coatings**This project is the result of an ad hoc collaboration between UCL and ICL. combining the development of photocatalystic antibiotic coatings to be used in medical devices and hospitals. and a unique approach to the synthesis of ZnO nanoparticle catalysts, for the synthesis of liquid fuels. This has shown that these ZnO nanoparticles are exceptionally efficacious when combined with the UCL photocatalytic polymer composite system. However, the mechanism underpinning this performance is not yet clear, and is intimately connected to the distribution of nanoparticles and organic dye within the surface of the polymer device, and its evolution over time. This project will apply advanced characterisation techniques to study this active surface, using cross-sectional microscopy, and depth profiling techniques (particularly FIB-SEM, SIMS and 3View). Since the ZnO particles are around 3nm, high resolution TEM / STEM will be required to explore the details of any dissolution over time, and the locus of dopant atoms. The student will gain a wide range of advanced characterisation techniques, as well as a grounding in organometallic chemistry, and antibacterial testing.
3. **Structural and compositional characterisation of resistive switching in silicon oxide (SiOx)**The objectives of this project are:

• To characterise by AFM & C-AFM changes in morphology and conductivity of SiOx during switching.

• To image conductive filaments using AFM & C-AFM.

• To characterise by SIMS the compositional changes during electroforming and switching.

• To perform In-situ biasing of oxides during SIMS analysis of electroforming and switching.

• To develop a model of the processes of electroforming & switching in terms of structural and chemical changes and the formation of conductive filaments.

The proposed project builds on a recent highly successful preliminary collaboration between the UCL and ICL groups that has demonstrated the inhomogeneous structure of resistive switching SiOx and its evolution during electroforming and switching. Resistive switching in SiOx is an exciting new phenomenon with huge technological potential. Resistive switching devices are components whose electrical resistance can be varied by up to 106 by an applied field. They are promising candidates for next generation electronic memories, offering significant advantages over Flash memory: very high packing density; fast switching; low energy; 3D integration, and ease of processing. However, the mechanism of switching is poorly understood. Although it arises from the formation of conductive filaments within the oxide, the nature of the filaments is not known. To understand this requires a comprehensive structural and compositional study of switching oxides – ideally with in-situ measurements of changes during filament formation.

1. **Making Crystals from Electrons**When electrons are spatially confined to form a one-dimensional system the electron energies can be described on the basis of a simple quantum particle in the box. However, it has been shown recently that as the width of the system increases the energies can be determined by the mutual repulsion of the electrons, when this occurs a single electron description is no longer adequate as the system is in a many-body state.
In these experiments the confinement is determined by voltages applied to split or patterned gates which gives rise to smooth variation in potential but with the disadvantage that changes in the gate voltage alters both carrier concentration and spatial extent. By producing a hard wall potential with AFM produced local anodic oxidation it is possible to maintain fixed width and vary the carrier concentration so allowing the dependence of the formation of the many-body state to be studied as a function of carrier concentration at constant width. For the first time the stability of the many body state can be investigated and predictions investigated as to the configuration adopted by the electrons as they move towards a Wigner Lattice or Electron Crystal.
(a) Surface gates are used to define a 1-D channel in a 2-D electron gas.
(b) Electrical transport data showing the onset of electron lattice formation.
(c) Surface gates will be replaced by side gates defined by AFM lithography to generate hard wall potentials.
2. **Spin Dependent Transport in Semiconductor Nanostructures**The spin-orbit coupling in semiconductor nanostructures has resulted in suggestions for spin dependent conduction in the absence of magnetic materials with possible spintronic applications. Although the effects are only observed at low temperatures the physical concepts which are acquired offer new perspectives for observing such phenomena at higher temperatures.
In this project the objective is to combine the spin-orbit interaction with the lifting of spin levels
due to the electron interaction in narrow channels. We will establish a spin lattice by means of sequential pairs of split gates, which, when appropriately biased, correspond to a synthetic gauge
 field in which the spin levels are modulated by application of a lateral voltage which allows the formation of an alternating spin-orbit field. The semiconductors utilised will be InSb, InGaAs and InAs quantum well heterostructures, patterned into nanostructures.
3. **Microdroplet-based nanoparticle characterisation**The project will be centred around the study of gold nanoparticles with tunable size, shape and surface properties at liquid-liquid interfaces. (3) A modular synthetic approach allows us to systematically tune structural properties and study effects on interfacial assembly and mechanically forced desorption. Integration into a microfluidic environment will also enable us to study nanoparticle-analyte interactions, e.g. for point-of-care drug monitoring or contamination detection in drinking water. Further insights on crucial parameters of interfacial assembly and disassembly may lead to align and deposit supra-colloidal aggregates and help us develop new fabrication routes for nanoscopic devices. A comprehensive portfolio of material characterisation techniques will enable the student to acquire a sound set of skills and get immersed in a very active and promising field of research.
4. **Peptide-targeted gold nanostars for treatment of Parkinson’s**Parkinson’s disease (PD) is currently costing the UK £14 billion/year in drug, care and lost income and projected to continue rising as life expectancy increases. Current PD therapeutic approaches do not stop neurodegeneration; hence effective neurorestoration is urgently required. Therapy with neurotrophic factors is hampered by their high cost, side effects, limited blood-brain barrier crossing and rapid degradation. Nanoparticles and small-size neuroprotectants may provide new means for the targeted delivery of neurotherapeutics. We have recently identified a small peptide (S100) capable of protecting neurons in brain injury models and in a cell model of PD. Here we propose to engineer efficient brain penetrable nanoprobes that will serve as a delivery vehicle for the neuroprotective peptide S100.
5. **Well-defined bionanomaterials for cancer immunotherapy**A major emerging field in medicine is adoptive cellular immunotherapy, where cells of the immune system are expanded and/or genetically engineered ex vivo before being returned to the body to fight diseases such as cancer or autoimmunity. Current experimental protocols largely rely on the stimulation of immune cells in vitro with very simple artificial materials, such as biofunctionalized polystyrene, however, these do not begin to approach the complexities of the in vivo environment, which is mechanically, chemically and topographically structured on the nanoscale. Improved therapies will be delivered by a next generation of biomaterials that imitate specific in vivo niches to give clinicians fine control over cell differentiation and function, generating bespoke therapies for particular diseases. The challenge is to carry out high-resolution multimodal characterization of the nanoscale structure of biomaterials, and to directly correlate these results with relevant biological readouts of how immune cells (particularly T cells) respond to these materials. This information will be applied in an iterative process to create successive generations of bionanomaterials that more faithfully replicate in vivo structures and deliver enhanced clinical function.
6. **In-operando evaluation of interfaces in all-solid state batteries**Solid-state Li-ion batteries (SSLBs) can increase safety, cycle life and energy density from conventional, liquid electrolyte-based Li batteries and so promote the development of a high performance and safe, electric vehicle-based automotive industry. This can be achieved by the use of solid electrolytes with high enough electrochemical stability window to allow Li metal and high voltage cathodes as electrodes. A key challenge is however the rather low power density due to slow Li+ ion transport through the solid electrolyte-electrodes interfaces and the low cycle life due to the propagation of Li dendrites through the solid electrolyte that eventually promotes the short circuit of the cell for currents of 0.5-1 mA/cm. The aim of this project is to quantitatively analyse and optimise the performance of 2D and 3D interfaces between the Li metal –based anodes and Li7La3Zr2O12 (LLZO) related garnet oxides. Bulk and surface-sensitive techniques will be used to evaluate the performance of the cells and the microstructural and chemical degradation of the interfaces under in-operando conditions.
7. **Microwave control over proximity induced superconducting spin triplet state**Spin triplet superconductivity can be induced in a neighbouring ferromagnetic layer in close proximity and this long range spin polarised supercurrent may have important applications in terms of cryogenic memory for quantum technologies. However, as yet proximity induced spin triplet superconductivity has been induced by creating a physical layer with inhomogeneous spin order at the interface between a superconductor (S) and a spin aligned ferromagnet (F). Static inhomogeneous spin state layers could be domain walls or artificial antiferomagnet multilayers for example. In this project we want to explore the possibility of inducing an inhomogeneous spin state in the time domain, which has been predicted theoretically but not demonstrated experimentally. The methodology will involve inducing ferromagnetic resonance in the ferromagnetic layer at microwave frequencies. The project combines film growth and device nanofabrication combined with advanced characterisation at cryogenic temperatures and in a microwave cavity (single frequency and dc magnetic field) or stripline (broadband methodology). The new dilution refrigeration capabilities at UCL providing 20mK and up to 40 GHz facilities will be utilised. Single superconducting (Nb or Al)/ferromagnet (Co) junctions will be examined in the first instance and in order to incorporate these into the microwave set up, planar structures will need to be fabricated to create ballistic point contacts.
8. **Photo-induced surface-enhanced Raman scattering for biochemical sensing**Surface-enhanced Raman scattering constitutes the backbone of optical fingerprinting of many relevant complex molecules, from plastic explosives to diseases agents, with the hallmark of providing both chemical specificity and high sensitivity, down to the picomolar regime and beyond. The latter is mainly achieved via an electromagnetic enhancement of Raman scattering, utilizing localised surface plasmon excitations in nanostructured metallic films or on metallic colloids. Since Raman scattering scales with the fourth power of the local field, large enhancements up to typical factors 108 to 1011 are possible. Much more elusive is an additional chemical enhancement of Raman scattering, facilitiated via charge transfer from the metallic nanostructures to the molecules under investigation. In a recent pioneering study, Parkin and Maier demonstrated that this chemical enhancement can be induced via UV illumination of titania substrates coated with metallic nanocolloids (Nature Communications 7, 12189, 2016). Crucially, the additional enhancements works for a large number of molecules, from plastic explosives to TNT and large biomolecules. With this studentship project we want to investigate the physical origin of this effect, named PIERS — photo-induced enhanced Raman scattering – further. We want to understand the physical mechanism of charge transfer, discover ways of tuning it, and optimize the conditions for chemical enhancement of Raman scattering utilizing a variety of metallic colloids under different illumination conditions. The effect will then be benchmarked for a number of defence-relevant substances at dstl.
9. **Characterising functional networks of nanotubes and graphenes**

Carbon-based electrodes promise both cheap, printable, flexible, transparent conductors and high performance thin film transistors, crucial for large area plastic electronics. A new process developed at Imperial/LCN/UCL allows dissolution of single-walled nanotubes, graphenes, and other 2d materials, without any damaging sonication or oxidation; thus, in principle, very long SWNTs and large flakes can be dispersed. The process produces charged nanocarbons, which are truly individualised in solution (as shown by neutron scattering), due to electrostatic repulsion. In addition, the charging process can be selective for metallic SWNTs, or semi-conducting SWNTs, and can be used to remove other unwanted impurities. The use of long, metallic nanotubes should provide the required significant improvements in transparent conducting network performance and electrochemical electrodes. The charge can be neutralised without damage, or exploited to control the deposition process, including creating hybrid composite films. The remaining semi-conducting SWNT fractions are of interest transistors and other PE applications; the LCN approach offers prospects of separating the semi-conducting species by band gap / type. Our SWNT separation/dispersion technology is already patented and has been licensed for commercialisation. The performance in application depends on the nature of the networks that form, whether predominantly two-dimensional for thin film electronics or 3 dimensional for electrodes; key factors include alignment, junctional density, junction conductivity, porosity, surface area, and roughness. Characterisation can be performed using conductive AFM in conjunction with device operation, polarised Raman microscopy, coupled SEM-Raman imaging, HAADF STEM tomography, and neutron scattering

1. **Solar cells based on two-dimensional monolayer materials “beyond graphene”**

Solar energy still provides a small fraction (~1%) of the present energy production. While solar energy harvesting technology can in principle cover the entire energy demands, the low efficiency results in high energy costs preventing a wider spread of the already developed silicon technology as well as growing organics-based solar cell technology. New efficient and low-cost materials are key to solving the challenging energy problem.

A range of new atomically thin materials, alike graphene but with direct band gap in the visible range, has started to emerge as a very attractive alternative for solar harvesting and light emitting [1]. These are the Group VIB of transition metal dichalcogenides (TMDs) and include: WS2, WSe2, MoS2 and MoSe2 [1]. In their atomically thin two-dimensional form they have an active direct band gap in the visible-near IR range (2 eV and 1.6 eV), they are stable in air, mechanically robust and flexible. They exhibit silicon-like carrier mobility and, despite their atomic-scale thickness, they absorb between 5-10% of incident light, more than an order of magnitude higher than the absorption in GaAs of comparable thicknesses. Significant research challenges nevertheless have to be overcome to see these materials in practical applications. They include (1) development of high-quality crystalline materials over large areas; and (2) optimisation of the process of photon conversion into charge carriers.

In this project we will develop new synthesis strategies using chemical vapour deposition to obtain continuous atomic layers of TMDs over large areas with controlled doping. This activity will take place in Dr. Mattevi’s laboratory (ICL), equipped with advanced material growth systems. In order to enhance solar harvesting efficiency, we will apply spatially and temporally resolved optical spectroscopy techniques to uncover the photon conversion process by tracking exciton dynamics in these materials as well as in fabricated devices. Spectroscopic studies will take place in Dr. Mitrofanov’s laboratory (UCL), where the spectroscopy system was recently developed to investigate exciton dynamics in organics-based light harvesting materials.

This project is matched with the UK’s commitment to solve the energy problem through research and development of advanced materials. The impact of this research will also extend to light emitting applications, where new advanced materials can improve reliability and reduce costs. The student is expected to gain the knowledge light harvesting technologies, material growth and device fabrication techniques, and optical spectroscopy methods.

Leading research institutions overseas will be involved in this project: present research collaboration with Nanyang Technological University (Singapore) will provide high-quality single crystal organic materials (rubrene) for research on light-harvesting efficiency improvement in organics, while collaboration with Los Alamos National Laboratories will complement the device fabrication and study. In order for the student to gain broader experience with material and device development, a placement in one of the institutions is envisaged.

[1]. L. Britnell et al. , Science 340, 1311 (2013)