Melbourne

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Melbourne – Keynote Abstracts

Characterization of physically robust hydrogels for biomedical applications

A/Prof. Michelle L. Oyen, Department of Engineering, East Carolina University

Biography

Michelle L. Oyen has a diverse academic background and wide-ranging interests in biomedical engineering, biomechanics, and biomimetic materials. She completed her Ph.D. in Biophysical Sciences and Medical Physics at the University of Minnesota in 2005 after degrees in Materials Science (B.S. 1996) and Solid Mechanics (M.S. 1998) at Michigan State University. She was a Research Scientist at the University of Virginia for one year before starting a faculty appointment at the Cambridge University (U.K.) Engineering Department in 2006. She returned to the U.S. in 2018 and is currently an Associate Professor of Engineering at East Carolina University. In her academic research, Michelle has over 100 journal publications, on topics as diverse as biomechanics of pregnancy, nanoindentation of hydrogels, and fracture of biomimetic tissue engineering scaffolds. Wearing her science communications hat, she has appeared on documentary television (NOVA, BBC), in public presentations (Cambridge Science Festival, The Hay Festival), in radio interviews (The Naked Scientists), in blog posts (Nature.com), and featured articles (The Guardian, The Conversation U.K.).

Abstract

Hydrogels have quickly become ubiquitous in biomedical research: as tissue engineering scaffolds, drug delivery applications, and as substrates for studying primary cellular function. Although promising because of their excellent cellular biocompatibility, many hydrogels have insufficient physical properties and are prone to brittleness. This deficiency is not observed in healthy soft biological tissues, arguing for a biomimetics approach to hydrogel development. There are also challenges inherent in characterizing the physical properties of hydrogels. In this context, two applications are featured in this presentation. First, the charged environment found in cartilage is replicated using polyelectrolyte hydrogels based on polyvinyl alcohol and polyacrylic acid. These materials can mimic the electrostatic stiffening behavior observed in natural tissue while demonstrating diminished fluid transport due to the electrical charges, depending on the hydrogel cross-linking method. Second, mimicking the biological nanostructure of collagenous soft tissues, weak hydrogels are reinforced with electrospun nanofibers. By imitating the cornea's laminated fiber architecture, dramatic improvements were found in both hydrogel strength and fracture toughness. These examples illustrate how creative biomimetic fabrication methods and composite materials strategies can be employed to design novel, robust hydrogels for demanding biomedical applications.

Using microfluidics to probe complex flows in biomimetic systems

Prof. Amy Shen, Micro/bio/nanofluidics Unit, Okinawa Institute of Science and Technology, Japan, https://groups.oist.jp/mbnu/amy-shen

Biography

Amy Shen is a professor in Micro/Bio/Nanofluidics Unit at Okinawa Institute of Science and Technology Graduate University in Japan. Her research is focused on microfluidics, rheology, and self-assembly, with applications in nanotechnology and biotechnology. She received the Ralph E. Powe Junior Faculty Enhancement Award in 2003 and the National Science Foundation's CAREER Award in 2007. Amy was also a Fulbright Scholar in 2013. More recently, she gave the 2019 Bergveld lecture at the University of Twente, Netherlands. She is an associate editor for Soft Matter, Micromachines, and Biomedical Microdevices.

Abstract

Microfluidics has emerged as a powerful tool in biotechnology research and for modeling various features of biological systems. My research group has recently experimented with microdevice fabrication using the subtractive three-dimensional (3D)-printing technique of selective laser-induced etching (SLE). SLE fabricated glass devices can sustain very high deformation rates without failing, provide access to little-explored flow regimes, and enable flow visualization from multiple planes of observation, allowing the quantitative study of 3D flow instabilities.

A glass microfluidic device containing free-standing microfluidic circular cylinders is fabricated and employed to model synchronized or coupled motions of motile objects (e.g., cilia) with a focus on viscoelastic fluid-structure interaction. Our studies demonstrate that slender bodies in viscoelastic flow can exhibit highly correlated dynamics and thus provide insight on analogous processes in biological systems.

Multifunctional Interfaces from Nature's Versatile Lubricant

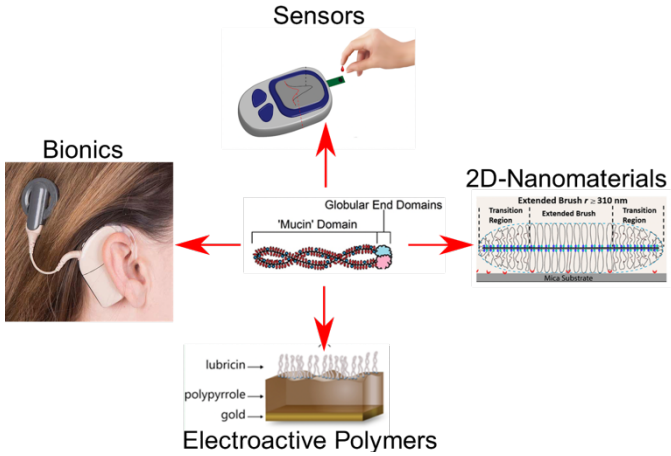
Dr George (Wren) Greene, Institute for Frontier Materials and ARC Centre of Excellence for Electromaterials Science, Deakin University, Melbourne, Victoria 3216, Australia

Biography

Dr. George "Wren" Greene began his research career in the R&D department of the Porex Corporation, the world's largest manufacturer of molded porous polymer materials that serves the industrial, biomedical, and healthcare sectors. Dr. Greene left Porex to pursue a PhD in Materials at the University of California, Santa Barbara studying under the late Professor Jacob Israelachvili who is widely regarded as one of the most influential experimentalists in the field of surface and interfacial phenomena. In 2011, Dr. Greene joined the Institute for Frontier Materials (IFM) at Deakin University and was awarded an ARC DECRA fellowship in 2013 to investigate the properties and potential applications of lubricin, a biolubricant and anti-adhesive glycoprotein having many interesting properties. Dr. Greene is currently a Senior Fellow in IFM and leads the advanced interfaces group that applies surface and interfacial science to create innovative, multifunctional, and responsive material technologies.

Abstract

Lubricin is a large mucin-like glycoprotein that is most well-known for the important role it plays in the boundary lubrication and wear protection of articular cartilage surfaces. However, lubricin possesses an impressive array of lesser-known properties including interfacial self-assembly, anti-fouling, size-selective transport, and high electrostatic charge density. Using lubricin self-assembly, virtually any solid interface can be rapidly and robustly modified with a versatile property tool-kit that both enhances and expands interface functionality. Here we highlight several recently developed lubricin enabled technologies applied to a diverse range of problems including improving the sensitivity and longevity of bionic neural interfaces, electrochemical and optical sensing within complex, highly fouling media, improving the stability of 2D-nanomaterial suspensions, and the fabrication of advanced electroactive polymer films.



Making and breaking capillary assemblies of colloids at interfaces under extreme deformation

A/Prof. Valeria Garbin, Department of Chemical Engineering, Delft University of Technology

Biography
Dr. Valeria Garbin did her MSc in Physics at the University of Padova and her PhD at the University of Trieste in Italy. She was a Rubicon fellow in the Physics of Fluids group at the University of Twente (Netherlands), and a postdoc at the University of Pennsylvania, before starting her research group at Imperial College London in 2012. She joined the Department of Chemical Engineering at TU Delft in 2019 as Associate Professor. Valeria has been awarded an ERC Starting Grant, was the 2018 recipient of the McBain medal (RSC/SCI), and is the 2020 recipient of the Soft Matter Lectureship of the RSC.

Abstract
High-rate deformation of soft matter is an emerging area central to our understanding of far-from-equilibrium phenomena during shock, fracture, and phase change. Monolayers of colloidal particles are a convenient two-dimensional model system to visualise emergent behaviours in soft matter, but previous studies have been limited to slow deformations. We have developed an experimental method to probe and visualise the evolution of a monolayer of colloids confined at a bubble surface during high-rate deformation driven by ultrasound. We observed the emergence of a transient network of strings, and used discrete particle simulations to show that it is caused by a delicate interplay of dynamic capillarity and hydrodynamic interactions between particles oscillating at high frequency. Remarkably for a colloidal system, we found evidence of inertial effects, caused by accelerations approaching 10,000*g*. These results also suggest that extreme deformation of soft matter offers new opportunities for pattern formation and dynamic self-assembly. For large deformations we also observed different mechanisms of disassembly, including particle expulsion and monolayer fracture.

Melbourne – Oral Presentation Abstracts

Metallo-nanodroplets for catalysis and nanostructure fabrication

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Surface nanodroplets are referred to small droplets with attoliter to femtoliter in volume and immobilised on substrates in contact with an immiscible liquid phase. The unique microenvironment of surface nanodroplets renders advanced features for miniaturising process and reactions with high efficiency.[1,2] The liquid-liquid interface between nanodroplets and surrounding phase allows for extended droplet lifetime as well as for reagents imparting from one phase to the other. Within droplets, reactions are compartmentalised and accelerated due to the high surface area-to-volume ratio of nanodroplets.[3]

In this work, we show *in situ* formation and assembly of gold-thiolate nanostructures in surface nanodroplets. Each droplet served as a nanocompartment to confine the nucleation and growth of the gold nanomaterials. The as-formed gold-functionalised droplets can facilitate a catalytic reaction,[4] leading to a fast fluorescent quench of Nile Red accumulated in droplets.

Moreover, we show that after exposure to air, the shrink of these gold-thiolate decorated droplets led to assembled gold-thiolate nanostructures on the surface. The composition of droplets and the substrate wettability are both key elements to alter these assemblies. The obtained gold-thiolate complex with active gold atoms can serve as scaffolds to enable the selective growth of gold spikes on the top, which have been regarded as favourable structures for surface-enhanced Raman scattering (SERS) substrates.[5] Our results here highlight the potentials of surface nanodroplets as novel miniaturisation platforms for nanomaterial synthesis, nanostructure fabrication, and catalytic reaction in nanoscale.

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Carboxylated nanocellulose superabsorbent for retaining soil water

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Water is critical for agricultural production and food security. Irrigated agriculture uses about 59% of the water available for human consumption in Australia. The efficient use of water resources is crucial for the long-term sustainability of the agricultural industry. Superabsorbent polymers (SAPs) appear as an attractive strategy to optimise water retention in soils. These are three-dimensional (3D) networks of linear or branched hydrophilic polymers with the capacity to absorb fluids at hundreds of time their own weight and remain stable. The majority of the commercially available superabsorbents are polyacrylamide or polyacrylate-based which are non-biodegradable. Here, carboxylated nanocellulose SAPs are presented as a renewable and sustainable alternative.

Different TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-oxidised nanocellulose superabsorbents were prepared using three different drying techniques: freeze-dried, and oven-dried at low and high temperatures. Soil was amended with different application rates of these superabsorbents to evaluate the effects on water retention, microbial community and their biodegradation. The absorption performance of nanocellulose superabsorbents is affected by the concentration and type of salts present in the soil water extracts. Oven-dried at 50 °C SAP presents the highest ionic sensitivity attributed to its large number of accessible carboxylate groups. The water retention of the soil treatments increases with increasing application rate. Soil treated with the freeze-dried superabsorbent shows the highest water retention, whereas those amended with the 50°C oven-dried SAP remain moist the longest. The biodegradation rate of these materials depends on the application rate and nutrient availability. Carboxylated nanocellulose superabsorbents emerge as high-performance biodegradable materials for agricultural use, able to replace the current non-biodegradable petrochemical-based superabsorbents.

Keywords: Carboxylated nanocellulose, TEMPO, soil water, superabsorbent, agriculture, hydro-retentor.

Separating macro- and nanostructure in fluctuation measurements of self-assembled lipid materials

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By correlating large ensembles of X-ray scattering data, fluctuation X-ray scattering can extract atomic and nanoscale structural information from a range of systems including colloidal glasses and crystals, liquid-crystal membranes, nanoparticles, and magnetic domains[1-4]. Real-space pair-angle distribution functions are higher order analogues of the basic pair-distribution functions and are rich in information about orientation and bond angles. This method maps fluctuations of scattered intensity into three- and four-atom correlation functions which encode two pairwise distances and one relative angle[5-7].

Here we present results of fluctuation scattering experiments on the hexagonal phase of a model self-assembled lipid system (CTAB-water). Using newly developed semiautomated algorithms for big datasets (>1000 patterns) we uncover a macroscopic preferred orientation effect which masks the nano-structural signal due to intensity fluctuations. Texture phenomena such as a preferred orientation, strain and peak broadening are commonly encountered throughout materials science. By simulating distorted datasets, we explore how correlation plots are altered by macroscale effects and present methods for disentangling structural information at these two length scales, broadening the range of materials and phase transitions amenable to fluctuation scattering analysis.

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Paper with tunable contact angles: fabrication of free-standing cellulose-based films with micropatterned features

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With the increase in consumer awareness of the environmental impact plastic-based products have on the natural environment, there is a huge drive to reduce our use of these products. Currently research is being undertaken to investigate more environmentally sustainable options. One of the options being pursued is the use of cellulose-based materials. These materials offer the great advantage of being produced naturally within the environment along with being recyclable, renewable and biodegradable. If they are to replace high precision plastic-based components in areas such as microfluidics, sensors and diagnostics, it is vital that these materials are able to be shaped and moulded in a reliable and cost-effective manner. Micropatterning with the use of nanocellulose fibres and cellulose nanocrystals (CNC) has been explored in this work.

Silicon moulds were created with photolithography and etching techniques. CNCs, with typical lengths of 100 nm were vacuum dried on top of the moulds. The nanocellulose fibres, with diameters last than 100 nm, were sprayed coated on top of create free-standing films. The micropatterns with channels widths between 1 and 500 μm and depths up to 10 μm are possible. Variations in the micropattern dimensions creates a material with a controlled surface roughness. Controlling these dimensions translates into the ability to tune the contact angle where a hydrophilic surface is able to be made hydrophobic in nature. This research serves as the foundation for a new generation of environmentally friendly cellulose-based microfluidic and diagnostic devices.

Deep eutectic solvents for cryopreservation

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Cryopreservation offers huge advantages in the medical field through the preservation of blood and stem cells, storage of reproductive cells, as well as the potential to store tissues and organs.[1] However, cryopreservation is limited by the available cryoprotectants (CPAs). Dimethyl sulfoxide (DMSO) and glycerol are the primary CPAs, but both can be toxic and require extensive washing of preserved cells before use.[2] Furthermore, there are some cell types that cannot be cryopreserved using these two CPAs.[1] Thus, there is a need for different, non-toxic CPAs, ideally with tuneable properties.[3]

Deep eutectic solvents (DESs) are a subclass of ionic liquids, many of which are non-toxic. Due to the extensive number of deep eutectic solvents, they offer a broad range of properties, so some may have the potential to be alternative CPAs. To date, only a very few studies have examined the cryoprotective applications of DESs, but these have shown comparable viability of cells stored using DESs compared to those stored using DMSO.[4]

We have explored the thermal properties of a number of DESs, including in combination with water to identify glass transition and recrystallisation behaviours. We have also studied the shrink/swell behaviour of cells (THP-1 cells) in the presence of DESs in order to measure the permeability of different DESs which gives information on their potential applications as CPAs. Finally, we have demonstrated successful cryopreservation of this cell type with a DES.

The results of this research could provide new avenues of cryopreservation which could be applied to cell types which can't currently be preserved with existing CPAs. This in turn would have wide-ranging benefits, especially in the biomedical field.

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Rational design of ultrashort Indolicin-inspired antimicrobial peptides and control of self-assembling properties

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Abstract

Antimicrobial resistance was described by the World Health Organisation as one of the main public health concerns of the 21st century that threatens the effective prevention and treatment of an increasing range of common infections. This data has led the scientific community to engage into research on alternative strategies to the traditional small molecule antibiotics. Antimicrobial peptides (AMPs) are produced by various organisms as part of their normal immune response. A growing number of these peptides have been shown to self-assemble into nanostructures that are thought to play a role in their antimicrobial activity and can be exploited to create biomaterials. While most of studies to date have focused on long peptide sequences and proteins, recent works demonstrated that short peptide sequences also self-assemble and display antimicrobial activity. For instance, battacin derivatives composed of only 3-5 amino acid residues can self-assemble, interact with bacterial membranes and display potent antimicrobial activity (1-3). Thus, we hypothesise that novel ultra-short antimicrobial agents can be rationally designed and that their antimicrobial spectrum of activity can be tuned with minimal sequence variation.

Here, we focus on Indolicidin ultrashort fragments and Fmoc derivatives containing 3 to 6 amino-acids residues. Minimum inhibitory concentration studies showed the influence of sequence length, amino acid content, amphiphilicity, net charge and polarity on the activity of these peptides against Gram positive, Gram negative bacteria and fungal species. A set of biophysical techniques, including Fourier transform infrared spectroscopy, small angle X-ray scattering, and electron microscopy showed that some of these designed antimicrobial peptides self-assembled into liquid crystalline beta-sheet nanofibrillar aggregates in aqueous media, resulting in the formation of hydrogels. The versatility of the formed nanostructures is well suitable for nanotechnology applications and those peptides could be used in the design of antimicrobial biomaterials.

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Antibacterial Gallium Liquid Metal Micro-/Nanodroplets

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Antimicrobial resistance (AMR) is one of the most significant health-related issues of the 21st century. It is a problem that necessitates the need for identifying alternative treatment technologies [1]. As a potential replacement for conventional antimicrobial agents, metal and metal oxide nanoparticles (NPs) have been studied. Additionally, the antibacterial effects of metal ions, such as silver, copper and recently gallium, have been demonstrated to be effective antibacterial agents: for example, gallium ions have been shown to exhibit significant efficacy in their ability to kill microorganisms through a “Trojan horse” mechanism [2]. However, there is limited research undertaken regarding the interactions taking place between gallium (as a metal) with pathogenic bacteria. Here, we demonstrate the antibacterial activity of gallium micro-/nanodroplets against the Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* bacteria. Additionally, when a surfactant is added to the particle system the antibacterial activity was found to be enhanced. We propose a novel antibacterial action via a unique material-biological interaction mechanism taking place between the liquid metal droplets and the bacterial cells. The knowledge gained through this work will inform the future design of antibacterial technologies, while also providing fundamental results pertaining to the interactions taking place between bacteria and liquid metals.

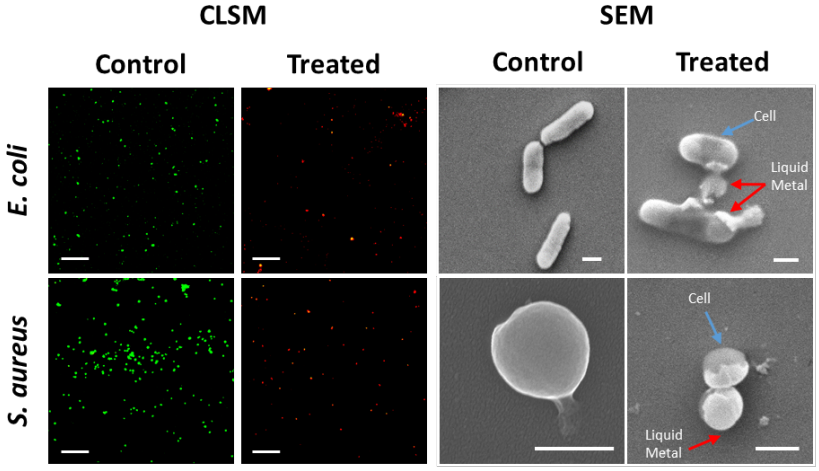

Figure 1. Confocal laser scanning microscopy images (left) showing predominately viable cells (green) in the control samples and inactivated cells (red) in the treated samples (Scale bar is 20 µm). Scanning electron microscopy images (right) highlighting the interactions between the gallium liquid metal droplets and *E. coli* and *S. aureus* (Scale bar is 500 nm).

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Designing Lipid Mixtures that Replicate Self-assembly in Different Types of Milk During Digestion

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Introduction: Digestion of the milk lipids in our intestines yields monoglycerides and fatty acids that self-assemble into a variety of liquid crystalline structures. This self-assembly process is species dependent,[1] suggesting an important role for these structures in infant nutrition. Our recent work has focussed on designing lipid mixtures that replicate the self-assembly of different natural milks during digestion and analysing how the self-assembled digestion products interact with biliary emulsions to influence nutrient activity.
Methods: Lipid mixtures were prepared by mixing either purified homotriglycerides or cow milk fat and canola oil. These lipid mixtures were dispersed to form milk-like emulsions or canola oil was mixed directly with cow's milk to generate milk-like emulsions. Coherent anti-Stokes Raman spectroscopy (CARS) microscopy was used to confirm mixing of the lipids into cow's milk and Small angle X-ray scattering with *in situ* lipolysis was used to measure the self-assembly of lipids in emulsions of the mixed lipids during digestion.[2,3]
Results & Discussion: The triglyceride composition of the digesting emulsions was found to be a primary driver of lipid self-assembly during milk digestion. By designing emulsions with the right balance of medium/long chain saturated lipids (more abundant in cow's milk) and long chain unsaturated lipids (more abundant in human milk), lipid mixtures could be produced that replicated both natural milks and infant formulae. The lipid self-assembly in mixtures of cow's milk and canola oil was found to replicate that of human milk when the right balance of these lipids was struck, irrespective of whether the lipids were pre-mixed and emulsified or whether the canola oil was dispersed directly into cow's milk. These mixtures provide simplified lipid compositions that can be used as milk mimics with tuneable colloidal structures to investigate the interactions of endogenous surfactants, lipophilic drugs and nutrients with milk in the gastrointestinal tract.

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The shape, size and diffusion of anisotropic nanoparticles near interfaces

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Engineered particles found in next generation solar cells, nano-electronics, photonic materials, and nano-sensors have experienced a rapid growth in research interest over the past decade. This is in large part due to improving techniques to control particle anisotropy in shape such as nano-rods, nano-plates, iso-hedras and nano-prisms, or to control anisotropy in material properties such as janus particles. Yet, direct force measurement methods including colloidal probe atomic force miscopy (AFM) and the surface forces apparatus, that provide fundamental insight into the interaction forces between particle, are often limited to micron scale or larger surfaces with flat or simple curvature. Thus, there is a need to see more quantitative methods capable of measuring interactions between anisotropic particles where the anisotropic nature of the particle is both more interesting and often critical to assembly.

We discuss the use of two new scattering methods to observes the size, shape and diffusion of label-free nanoparticles (*e.g.* Janus particles, ZnO nanorods, carbon nanotubes) near interfaces with nanometre resolution. The utility of conventional optical tools for probing these systems is limited by the proximity of an interface and the presence of particle anisotropy; yet it is the influence of these factors that makes such systems interesting, introducing asymmetric interfacial forces and separation-dependent hydrodynamic hindrance in each of the spatial modes of diffusion. We simultaneously record the spatially correlated scattering of multiple evanescent light sources by isolated anisotropic particles, and use this data to reconstruct instantaneous shape, positions and orientations at millisecond time-intervals. By observing diffusion in each spatial mode over time we are able to quantify each translational and rotational diffusion coefficient as a function of interfacial separation. Aside from fundamental applications, this approach will be particularly useful for understanding and tuning the self-assembly of films and other structures incorporating anisotropic nanoparticles.

Dynamics and Behaviour of Ultra-Small Gold Nanoparticles at the Supported Lipid Bilayer Interface.

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Nanomaterials - materials with nanoscale dimensions - are widely investigated in the scientific and medical communities and are of interest in many biological settings. The commonality between all applications is that they utilise the nanosized features of the material, specifically their departure from traditional bulk-like properties. In general, nanoparticle-based technologies must interact with, and often cross, a cellular membrane to be useful. To study cell-nanomaterial interactions, model systems are often used, such as supported lipid bilayers (SLB) which act as an archetypal bio-membrane. In this work, we investigate the behavior (dynamics, adsorption, translocation, and physical interactions) of ultra-small gold nanoparticle (AuNPs) with a SLB of 1,2-di-(9Z-octadecenoyl)-sn-glycero-3-phosphocholine (DOPC) supported by muscovite (mica), an atomically smooth, phyllosilicate substrate. A combination of small-amplitude - atomic force microscopy (AM-AFM) and molecular dynamics (MD) simulations were used to study the fundamental behaviour of the AuNPs at the biomembrane-liquid interface. The precise mechanism by which the AuNPs adsorb to the bio-membrane was elucidated, revealing several interesting behaviors: 1) initial adsorption, 2) nanoparticle incorporation within the bilayer, and 3) two-dimensional (2D) translocations within the upper-leaflet of the DOPC bilayer. These interactions are of broad scientific and medical interest because nanomaterials have recently become a viable method for manipulating matter at the cellular level, particularly for therapeutic and diagnostic applications.

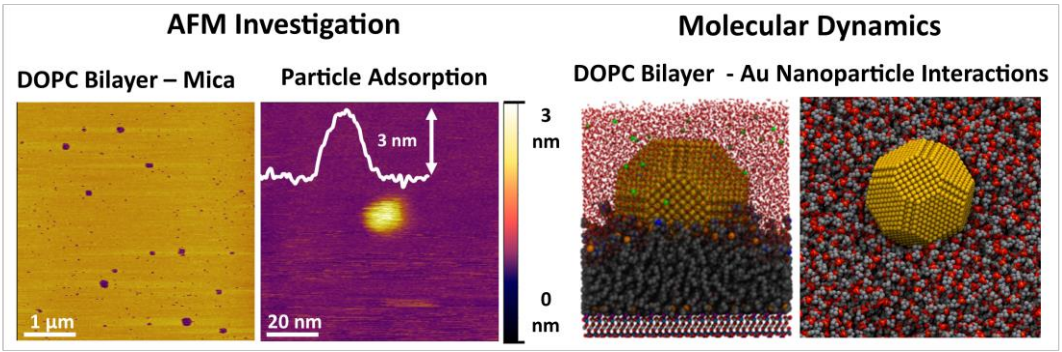

Figure 1. AFM and Molecular dynamics simulation investigation of the interaction of 5 nm AuNPs with a supported DOPC lipid bilayer formed at a mica surface.

3D printing with colloidal particle pastes using aqueous suspension-oil formulations

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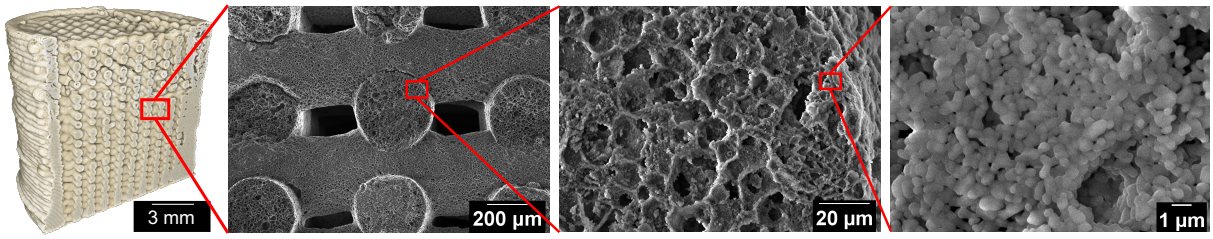
We present an approach to producing multiscale porous ceramics by 3D printing colloidal particle containing pastes. Millimeter scale porosity is created by the 3D printed scaffold strands. We introduce 20 micron scale porosity into the scaffold strands using paste formulations where the particles are in aqueous suspension and oil is added to create pores via either particle stabilized emulsions or capillary suspensions. Using this approach porous ceramic strands can be 3D printed *via* the Direct Ink Writing (DIW) technique. Micron scale porosity can also be developed by partial sintering of the ceramic. The rheological (flow) properties of the emulsion or capillary suspension pastes such as storage modulus and yield stress must be carefully controlled to produce paste inks suitable for printing by extrusion through the needle of the 3D printer. Control of the internal strand microstructure between particle stabilised emulsions and capillary suspensions is possible by controlling the amount of oil, surfactant and dispersant concentration. The objects become strengthened by sintering at high temperature. Formulations have been developed for alumina,[1] ultra-high temperature ceramics and bioceramic materials. Complex shaped objects can be printed and sintered into crack free components, but distortion during drying and sintering lead to poor shape and tolerance control. X-ray tomography is used to characterize the internal structure of the printed components. 4 point bend strength measurements demonstrate high strength to density ratio.



Multiscale structure produced in alumina.[1]

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Quasiperiodic Light

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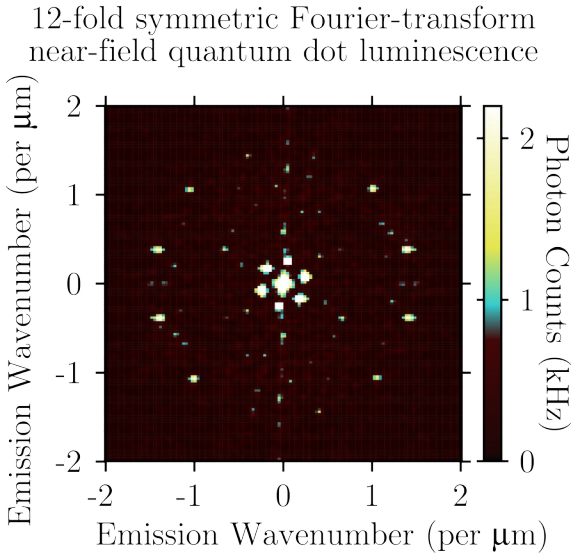
Quasiperiodicity is a form of spatial order which is observed in quasicrystalline matter. We construct a quasicrystalline metasurface out of a light emitting diode.[1] Using near-field scanning optical microscopy, we directly image the light field at the surface of the diode in three dimensions with superresolution. The reciprocal space representations of the images show that the light field is quasiperiodic. Periodic ordering is limited to at most 6-fold symmetry. This experiment demonstrates a light field with 12-fold symmetry.

The metasurface is a quasiperiodic arrangement of holes. The holes are filled with quantum dots. Energy is transferred from the light emtiting diode to the quantum dots, resulting in luminescence. Using spatially aligned near-field microscopy images, we contrast the blue emission of the diode inverse quasicrystal with the yellow emission of the quantum dot direct quasicrystal.



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High-water-holding pectin-based robust hydrogels with self-healing, biocompatible and anti-bacterial properties for drug-delivery

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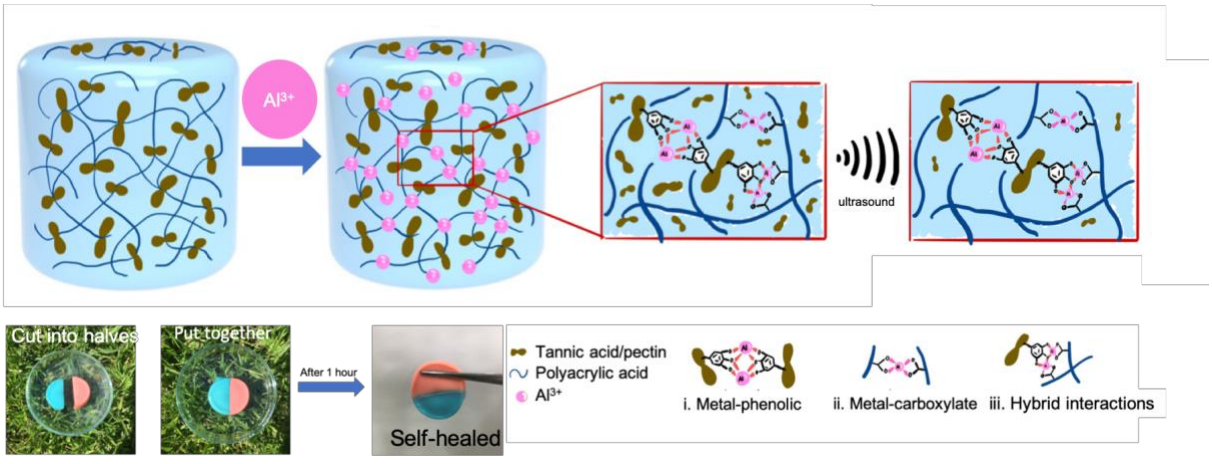
Despite the emergence of new technologies and the recent extraordinary progress in creating biopolymer-based, self-healing hydrogels, there is still an increasing demand for materials possessing multifunctionality, better mechanical properties as well as ideal biocompatibility. In order to solve this issue, we designed a pectin-based hydrogel with interesting properties by constructing a double-network structure using a small amount (15 wt %) of polyacrylic acid (PAA) with pectin, and introducing tannic acid (TA) as a functional component. This material has a high water-holding capacity due to the intrinsic hydrophilicity of pectin. The tough and self-healing structure can be attributed to the carboxylate groups from pectin and PAA, the combination of which was used to create both permanent and dynamic networks, based on ionic interactions with aluminium ions and hydrogen bonds. Meanwhile, TA plays a major role in reversible interactions within the hydrogel network, while acting both as a natural anti-bacterial and anti-inflammatory agent. The dynamic metal-phenolic linkages between aluminium ions and catechol groups of TA allow effective sustained (ambient) and ultrasound-enhanced release of TA. The inherent biocompatibility of these natural biopolymers, constituting the hydrogel, endows this system with outstanding cell viability and anti-bacterial properties simultaneously. We anticipate that this versatile pectin-based drug-delivery hydrogel is an ideal candidate for a wound-healing material in medical fields. The results of this work also provide insights into combining and processing naturally derived biopolymers for fabricating new materials to promote the use of sustainable resources and green chemistry.



Solvent effects of protic ionic liquids on proteins

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Protic ionic liquids (PILs) are cost efficient "designer" solvents which can be tailored to have properties suitable for a broad range of applications. PILs are also being combined with molecular solvents to enable more control over the solvent environment, driven by a need to reduce their cost and viscosity. I will discuss how we are using our understanding of PIL-water solvent properties[1] to design and characterise solvents for biological molecules. In particular, we are targeting being able to control protein solubility and stability, which are critical for applications in bioprocessing, biocatalysis, protein crystallography and cryopreservation. We have explored lysozyme and green fluorescent protein as model proteins in various PIL-water systems, using spectroscopic techniques and small angle x-ray scattering (SAXS)[2]. From this we have been able to identify which PILs are more biocompatible, and to identify specific conformational changes of lysozyme due to the presence of PILs. More recently, protein crystallography has been used to identify specific binding sites of the PIL ions and water to lysozyme.

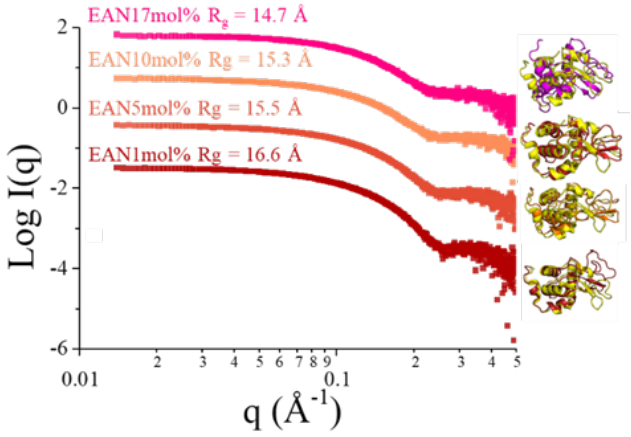

Figure 4. *SAXS patterns from the Australian Synchrotron using plate-based autoloader for lysozyme in varying concentrations of ethylammonium nitrate-water, including refined structure and comparison to the pdb crystal structure for lysozyme.*[2]

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Self-Assembly of Lubricin (PRG-4) Brushes on Graphene Oxide Affords Stable 2D-Nanosheets in Concentrated Electrolytes and Complex Fluids

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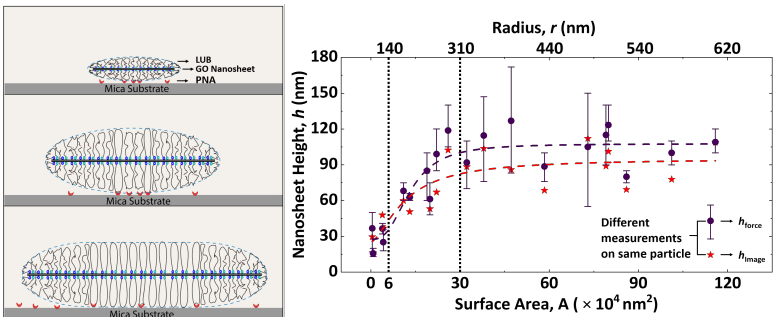
Graphene oxide (GO) and other 2D-nanosheet materials exhibit a range of useful physical, chemical, electrical and optical properties that may usher in the next generation of biomedical, bioimaging, or sensing technologies. One limitation of GO is its poor stability in concentrated electrolytes and other complex fluids that requires steric stabilizers, including surface grafted polymers, to overcome attractive Van der Waals interactions. Here we describe a simple, rapid, and highly effective method of modifying GO and other 2D-nanosheets with thick, grafted (bio)polymer brushes via the solution self-assembly of lubricin (LUB; a.k.a. PRG4), an antiadhesive glycoprotein. Atomic force microscopy (AFM) imaging and force measurements were used to characterize the morphology and nanomechanical response of these LUB-GO, 2D-nanosheet complexes (2D-NSC). These characterization studies reveal a strong correlation between the GO surface area and the thickness (i.e. molecular extension) of the grafted LUB brush caused by edge free volume effects. Likewise, this edge free volume influences the extension of the LUB brush structure more than 300 nm away from the edge resulting in a transition region of increasing brush extension before reaching a fully extended state within the central regions of the 2D-NSC. Fitting AFM normal force measurements using an adapted Alexander-de Gennes polymer brush model also indicates that the edge free volume leads to a mechanical softening of the LUB brush due to the lateral spreading and/or deflection of LUB molecules under compression. Finally, stability studies of 2D-NSCs dispersed in concentrated electrolyte solutions demonstrate the effectiveness of the grafted LUB brushes at inhibiting aggregation even in the harshest environments. These results provide strong evidence of LUB coating in the use of 2D-Nanosheets stabilizer, and the 2D-NSC in the applications such as biolubricant for contact lenses, optical sensor and bioimage sensor.



Absorption kinetics in Nanocellulose Foam: Effect of absorbate and surface charge

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Fluid absorption in nanocellulose foams follows two major stages: wicking and foam/fibre swelling. Wicking is the rapid flow of a fluid into the pores of the foam, driven by capillary forces. The second phase, fibre swelling, involves diffusion of the fluid through the foam, driven by an osmotic pressure difference. The superabsorbent characteristics of nanocellulose foams depend on a combination of variables. The absorption capacity and kinetics is affected by factors including cellulose composition, surface area, porosity and fibre surface charge of the nanocellulose, and solution being absorbed. In this study, we have quantified the absorption capacity and kinetics for different surface charged nanocellulose foams and compared the absorption capacity in fluids of different ionic strength. We found that nanocellulose foam absorption capacity in water is 25% higher than in body fluids, modelled with a 0.9wt% saline. The high surface charged foam shows a slower absorption kinetics in water due to difference in capillary action and foam structure. The high surface charged foams display a lower porosity than the low surface charged foams as quantified by X-ray tomography. Because of lower pore sizes, absorption kinetics is slower in high surface charged foams. In saline, both foams show similar kinetics- irrelevant of charge. The absorbed area of the foam (Figure 1) is quantified by image analysis and shows consistent results with absorption kinetics. These new nanocellulose superabsorbent are biodegradable and fully renewable; they present an attractive alternative to the current commercial polyacrylic acid based superabsorbent used in diaper and food packaging.

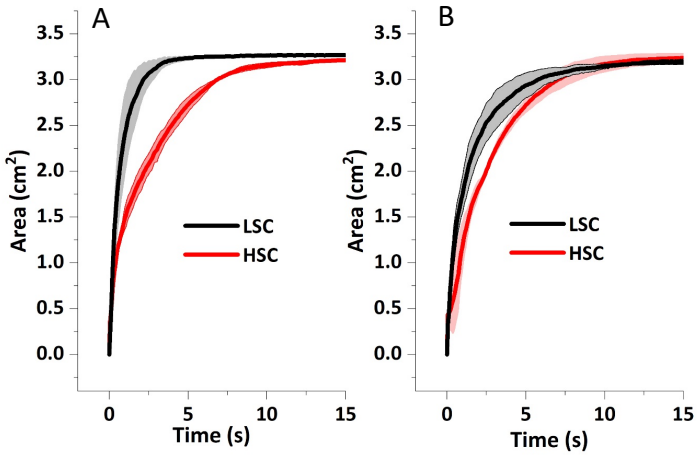

Figure 1: Effect of surface charge on absorbed area over time for LSC and HSC nanocellulose foams (A) milli Q water and (B) 0.9wt% NaCl.

Droplet Microfluidic SANS for interfacial coatings of soft matter systems

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Polymers and surfactants are commonly used to control the phase behaviour, stability, rheology and most importantly function of formulated products such as shampoos, pharmaceuticals and paints. Understanding how they interact and complex at the interface is critical to enhancing and refining the function of these multi-component emulsions. Measuring the structural properties of polymer-surfactant complexes at liquid-liquid interfaces is non-trivial, typically requiring well-defined and stable emulsions to perform scattering techniques such as small angle neutron scattering (SANS). However recent exploration into combined drop-based microfluidics and scattering techniques have emerged, introducing with it a new generation of microfluidic systems capable of measuring the structure, interactions and kinetic processes of the materials within emulsions. This presentation will explore the use of a novel microfluidic device for performing droplet microfluidic SANS with the purpose of analysing adsorbed layers at the drops interface and their structural confirmation while under flow. SDS and PVP in single and two-phase flow is analysed to understand the molecular structuring of the molecules with increasing degrees of complexity.

Investigating the Spatially Dependent Properties of Plasma Polymerised Acrylic Acid Films

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Plasma polymer films have been deposited on planar surfaces for a wide variety of applications, such as controlling cell growth or adding anchor molecules for biosensors. They can however also be deposited onto three dimensional objects, such as tissue engineering scaffolds, biomedical implants or 3D printed devices. Coating three-dimensional objects however is more complex as greater monomer fragmentation occurs closer to the electrode. It is therefore important to understand the properties of the plasma polymer films deposited at varying distances from the electrode. The use of plasma polymer films in biomedical applications also requires suitably stable films under physiological conditions, which will also be influenced by the distance from the electrode. Significant changes in film properties in aqueous conditions have serious implications on the incorporation of these films into a number of devices.

Acrylic acid is a commonly used monomer for plasma polymerisation to produce negatively charged carboxylic acid terminated surfaces, which have been used for a number of biomedical applications by manipulating cell growth. To gain a greater understanding of the spatially dependent behaviour of plasma polymerized acrylic acid (ppAAc) films deposited in our custom-built stainless steel T-shaped reactor, ppAAc films were deposited at varying distances from the electrode (3 – 19 cm) at different deposition powers (5 – 80 W). The surface chemistry was analysed with X-ray photoelectron spectroscopy while the film thickness was determined using spectroscopic ellipsometry. Film swelling of a selected group of samples was investigated with neutron reflectometry. Aqueous stability was investigated via immersion in Milli-Q and phosphate buffered saline. The film thicknesses and aqueous stability decreased while the carboxyl group concentrations increased as the distance from the electrode increased and/or the deposition power decreased due to reduced monomer fragmentation further from the electrode and at lower powers. For films deposited 11 cm from the electrode, complete film loss occurred at 20 W with film swelling at 30 W but no swelling at 40 W. This work highlights the importance of having a spatially well characterised plasma reactor to enable the deposition of plasma polymer films with the desired properties, which has significant implications on the incorporation of these films into a number of applications.

Linking structure to flow behaviour for wormlike micelles using rheology coupled small-angle neutron scattering

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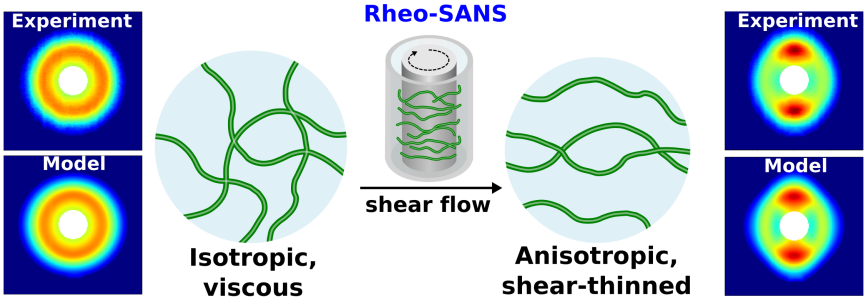
Wormlike micelles (WLMs) are self-assembled, thread-like surfactant aggregates that, at sufficiently high concentrations, entangle to form a highly-viscous mesh. Above a critical shear rate, this mesh disentangles and aligns with the direction of flow, causing a decrease in fluid viscosity (figure, middle). This shear-thinning property of WLMs is exploited in drag reducing agents, fracturing fluids, and personal care products such as body wash. However, despite their ubiquity, few studies have investigated mild, non-toxic WLMs, such as those formed by cocamidopropyl betaine (CAPB) and sodium laureth sulfate (SLES), at concentrations relevant to industry formulations.



We used combined rheology and small-angle neutron scattering (rheo-SANS) to explore the shear-induced alignment of wormlike micelles.[1] Shear-induced structural rearrangement and alignment of CAPB/SLES WLMs on a sub-micron range was observed as anisotropic lobes in rheo-SANS patterns (figure, right). To quantify these observations, we modelled WLMs as interacting, rigid cylinders over a local length scale with alignment determined by a Gaussian distribution of orientations centred along the flow direction, known as ϕ_{pd}. Where present, shear-banding was accounted for by summing isotropic and anisotropic patterns appropriately weighted by a fitted parameter (band value). Using this approach, we find that shear-thinning in anisotropic regions is correlated with a decreasing trend in ϕ_{pd} that is predominantly controlled by local interactions and volume exclusion effects, rather than global connectivity along the micellar contour.[1] This study provides a means to analyse and quantify the structural basis of complicated flow behaviour to directly link it with macro-scale function. This could fundamentally change our formulation methods using WLMs, incorporating a far more targeted and rational design approach.

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Snapshot measurements of liquid structure in 3D with an x-ray laser

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The 3D intermolecular structure of liquids is largely inaccessible to current x-ray scattering techniques because it only persists over sub-nanometre distances and sub-picosecond timescales. Emergent x-ray free-electron lasers can produce ultrabright femtosecond pulses that outrun the diffusion of molecules in a liquid and potentially probe the local 3D structure. However, even with these ultrabright x-ray sources the 3D information is encoded in a very weak diffraction that is buried in the noise. Here we report on attempts at proof-of-principle experiments to extract the 3D signal from the order of 10^5 x-ray laser diffraction patterns with advanced statistical methods[1-2]. Our goal is to recover a three and four-atom correlation function known as the *pair-angle distribution function*[3-4], which contains triplet correlations and bond angles. We have demonstrated our technique on lipidic cubic phases at nanometre length scales at the Australian Synchrotron[4]. The liquid experiment, however, is significantly more challenging and would open up a new capability for x-ray free-electron laser facilities to study liquid phases, supercooling and liquid-solid transitions.

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Predicting aqueous solubility by QSPR machine learning modeling

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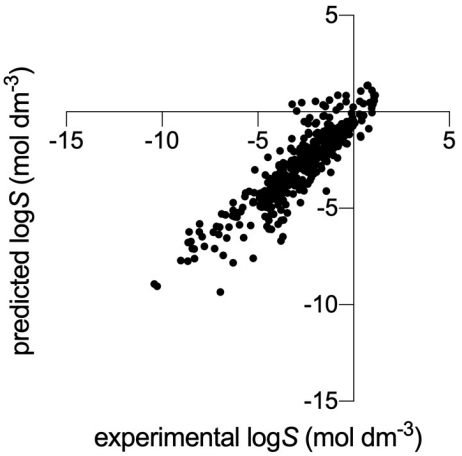
Aqueous solubility can be predicted using machine learning techniques. Using quantitative structure property relationship (QSPR) models, we examine whether descriptors that individually yield favorable models for the prediction of the Gibbs energy of solvation and sublimation can be used in combination with octanol-water partition coefficient to produce QSPR machine learning models for the prediction of aqueous solubility. Based on this strategy, applied to seven distinct datasets, all models exhibited an R^2 greater than 0.7 and Q^2 greater than 0.6 for the estimation of aqueous solubility. We also determined how uncoupling the descriptors used to create QSPR models in the prediction of Gibbs energy of sublimation yielded an improved model. Model refinement using an artificial neural network applying the same descriptors generated significantly better models with improved R^2 and standard deviation.



Nano-architectonics colours of photonic crystalline & amorphous assemblies of nanostructures

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This study aims to understand the mechanisms of structural colour originated from the nanoscale long- and short-range ordered assembly. Unlike the colours produced by pigments, in the nano-architectonics of photonics materials the structural colours are produced by the physical interactions of light with nanoscale structure arrangement[1]. The crystal-like long range ordered assembly of nanostructure produces angle dependent iridescent colours; the colour changes with the angle of observation or illumination. The colour appears due to interference of light coming from periodic arrangement of nanoparticles. On the contrary, the non-iridescent colours are angle dependent and produced by short range assembly of nanostructures. The transition from long range ordered assembly to the short range ordered assembly leads to suppression of the interference of light and enhancement of the coherent scattering at particular wavelengths.

Light interacts differently with different shape, size and arrangement of nanostructures and their assemblies. In this study, rod-shaped cellulose nanocrystals (CNC) and spherical Silica (SiO_2) nanoparticles are used to produce free standing films. Separately, both CNC and SiO_2 form long range ordered transparent films due to their high negative zeta potential. However, upon mixing at different ratios, opaque white colour films are produced which resembles the multiple reflections in the film. The CNC-SiO_2 composite sheets sustain different domains of CNC, SiO_2 and CNC-SiO_2. The domains size is of the order of visible light wavelengths. Therefore, the incident visible light wavelengths reflect differently from different domains and produce a white colour. The light wavelength interacts via a combination of different mechanisms like interference, coherent and incoherent scattering, diffraction, reflection and refraction[2].

The goal of this study is to understand and control the different fundamental mechanisms of nanostructure assembly and light-matter interactions which produce structural colours. The project is targets new knowledge with a focus on developing products of controlled optical properties for catalysis, sensors, bio-diagnostic and technological applications that are novel, low cost, biocompatible, highly efficient, and biodegradable. Furthermore, a strong fundamental knowledge of nano-architectonics of photonics materials helps mimicking and understanding the natural colours in birds, minerals, insects, plants, fruits and flowers.

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Investigating the self-assembly of short peptides: From amyloid disease to bioprinting

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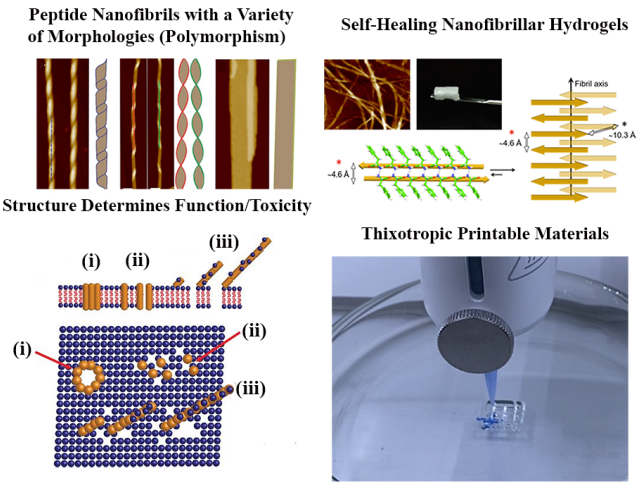

Many misfolded proteins or short peptides can self-assemble in aqueous solutions into β-sheet rich amyloid-like nanofibrils. These nanofibrils can be classified as 'toxic', 'functional' or 'synthetic'. Toxic nanofibrils are the hallmarks of diseases, including neurodegenerative conditions like Alzheimer's and Parkinson's and genetic conditions such as systematic hereditary amyloidosis[1] and phenylketonuria. Functional amyloids have physiological roles in a range of organisms including humans[2] and 'synthetic' amyloids are finding applications in a range of technological fields.

Whilst these nanofibrils all share many biophysical properties, in-depth investigations into their assembly mechanisms, molecular structures, nanoarchitectures and mechanical properties will help us distinguish subtle differences between these classes of amyloids. In this talk I will describe examples where we used a combination of nanoanalytical techniques and molecular simulations to begin to uncover differences between these different nanofibrils, and discuss how these maybe exploited to fight disease or develop new printable materials.[3]

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Cuboplex-mediated non-viral delivery of functional siRNA to Chinese Hamster Ovary (CHO) cells

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Lipid nanoparticles of internal cubic symmetry, termed cuboplexes, are potential non-viral delivery vehicles for gene therapy due to their "topologically active" nature, which may enhance endosomal escape and improve delivery outcomes. Within gene therapy, RNA interference (RNAi) therapy targets the knockdown of specific genes via the cellular delivery of siRNA. However, the clinical use of genetic molecules for therapeutic purposes has been limited by the low efficiency of delivery to the target cells without vectors, which remains a key challenge in gene therapy[1]. To enable the continued therapeutic application of siRNA, a suitable vector is required to (i) shield siRNA from degradation during cellular entry (ii) facilitate cellular uptake; and (iii) release siRNA intracellularly so that it will be accessible to the cellular machinery. In this study, we have used cationic cuboplexes, based on monoolein (MO) doped with a cationic lipid, for the encapsulation and delivery of anti-sense Green Fluorescent Protein (GFP) - small interfering RNA (siRNA) into Chinese Hamster Ovary (CHO) - GFP cells. An improvement in knockdown efficiency (~13 %) relative to the commercially available lipofectamine, and controlled release of anti-sense GFP-siRNA into the cell over a 72 h time period exemplifies the potential of these nanoparticles as novel non-viral delivery vectors for anti-sense GFP-siRNA (Fig 1).

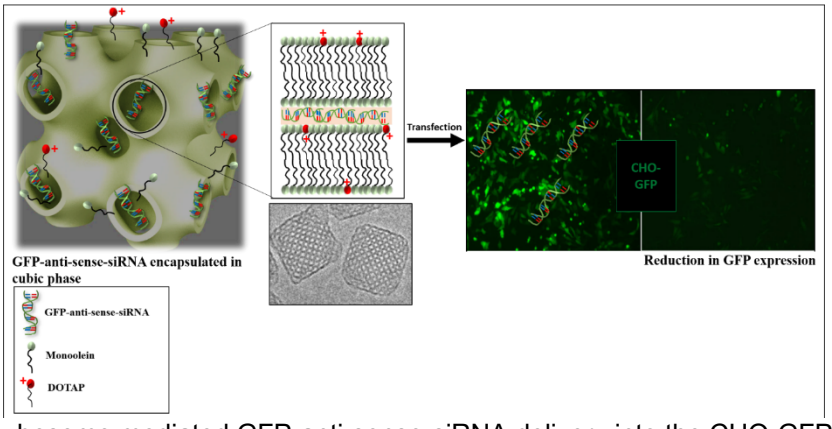

Fig 1. Cationic-cubosome mediated GFP-anti-sense-siRNA delivery into the CHO-GFP cell

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Polarisation engineering through polymer-nanomaterial interfaces

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Piezoelectric polymers intercovert between mechanical and electrical energies enabled by; (1) chemical dipole anisotropy on the polymer backbone; (2) polymer crystallisation, where these dipoles are aligned in a single domain; and (3) polarisation, where the direction of the net dipole in each crystal domain is aligned.[1]

Research has traditionally focussed on either increasing the dipole anisotropy, through chemical functionalisation (e.g., changing polyvinylidene difluoride (PVDF) to polyvinylidene difluoride-co-trifluoroethylene (PVDF-TrFE)), or increasing the crystallisation of piezoelectric phases. Polarisation has nearly exclusively been achieved by applying a high electric field (100 MV m^{-1}) at high temperatures (near the polymer Curie temperature) and has received minimal study over the past decades, despite limiting piezoelectric polymer performance due to dielectric breakdown.

Recently, we demonstrated polarisation engineering in PVDF-TrFE simply by controlling the interface between anisotropic nanomaterials (e.g., Carbon Nanotubes [2] or MXenes) with the PVDF-TrFE. The ability to engineer polarisation is enabled by the formation of polymer-nanomaterial colloids in solution, which then undergo shear alignment during film deposition, leading to large net polarisation.

In this presentation, I will discuss the principles enabling this polarisation engineering, and how by manipulating the polymer-nanomaterial interface we can develop next-generation piezoelectric energy conversion devices.

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Crusty Scum Model

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In a range of applications, solid particulates float to the surface of a container and form a continuous concentrated cream layer. An example of a cream layer, and the motivation for this work, is the scum layer that forms in anaerobic lagoons, which are ponds used in wastewater treatment to reduce nutrient loading in effluent. In anaerobic lagoons, fats, oils and greases float to the surface since their density is less than water. In addition, particles denser than water can be pushed upwards by convection if there is turbulence and eddies, or buoyed and floated by biogas produced from anaerobic digestion. The scum layer grows and consolidates with time. If the scum is too thick or impermeable, the top of the layer can dry and crack. A thick scum is required in uncovered lagoons to trap odorous gases, but in large covered lagoons, the scum layer can build to be metres thick, reducing operating capacity, inhibiting biogas transport and causing a hazard to lagoon covers. Understanding scum formation and mechanical behaviour is necessary for minimising scum build-up or optimising scum removal.

In related unpublished work to understand scum material behaviour, our colleagues and us show that scum is mostly floated sludge that forms a compressible porous network, and have measured scum rheological and dewatering properties. Based on this behaviour, in this work we propose a one-dimensional steady-state compressional rheology[1] model for scum consolidation due to buoyancy of accumulated solids and evaporation from the scum surface. We can account for the contribution to buoyancy from trapped gas either by assuming macroscopic bubbles under the scum layer or a distribution within the scum. The onset of desaturation is at the intersection of material compressibility and pore capillary pressure[2]. Upon further solids accumulation, the top of the scum forms a desaturated crust, which dewaters according to partially-saturated pore flow[3]. With appropriate material properties, the model enables prediction of the amount of scum required for the scum layer to consolidate to given concentrations and saturations. This then gives direct insight into lagoon operational issues such as the height that the scum sits above the waterline, adherence to covers, scum strength and how it may break up, and whether broken scum will sink.

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Low density metal core-shell particles for liquid marble formation

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From particle transport to separation and liquid stabilisation, particle encapsulation of liquid droplets has been examined extensively. An area more recently gaining attention is that of liquid marbles, and here, more specifically using electrostatics in the formation process.[1] Previous work has focussed on understanding the impact of material properties on particle transport and liquid marble formation within an applied electric field, using model particulate systems. Spherical, monodisperse samples of polystyrene (PS) with diameters between 20 and 140 μm have enabled assessment of the impact of material properties such as density and size on the particle extraction ability and stabilisation capabilities.[2]

Cohesion and conductivity of PS particles had previously been altered through the addition of polypyrrole (PPy) with various dopants to study the impact of a range of these two parameters.[3] Metal deposition onto colloidal template surfaces is well established[4] and has also recently been successfully demonstrated for liquid droplets.[5] We have used this method to coat the model PS particle surfaces with a film on nickel. Herein, we compare the extraction of these increasingly conductive nickel-PS composite particles to previous studies[3,6] and examine the stability of the resulting particle-stabilised liquid droplets.

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Surfactant-free techniques for nanoparticle deposition using hydrotropes

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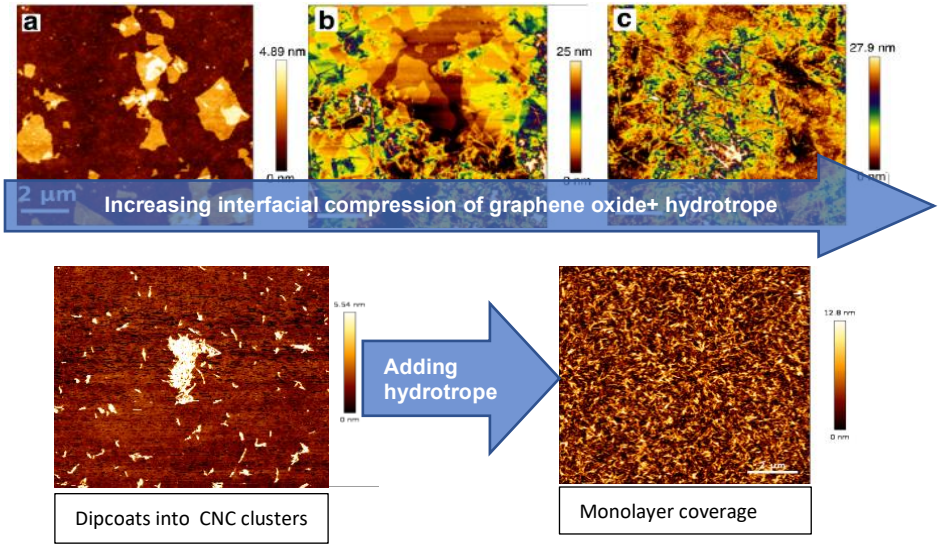
When nanomaterials such as graphene oxide nanosheets or cellulose nanocrystals adsorb to the air-water interface, they can be transferred to a substrate through dipcoating, imbuing the substrate with their characteristics. Surfactants are often added to these systems, adsorbing to the nanoparticles in order to facilitate this spontaneous adsorption to the air-water interface. Surfactants can however be environmentally harmful and difficult to remove after use, impacting the behaviour of the final coating. As an alternative, we have investigated the use of smaller amphiphilic molecules called hydrotropes, which are widely applied in industry as solubilizing agents but are poorly understood at a fundamental level. In particular, very little focus has been previously given to their promising interfacial behaviour.

We demonstrate, for the first time, that hydrotropes facilitate the dipcoating of the 2D material graphene oxide, with the nanoscale texture of the coating being modified through interfacial compression.[1] These hydrotropes also provide a surfactant-free, scalable method for the monolayer deposition of cellulose nanocrystals (CNC). In order to better understand these processes, in conjunction with atomic force microscopy examining the final coatings, we probe the behaviour of the nanoparticle-hydrotrope assemblies right at the air-water interface using surface pressure tensiometry and X-ray reflectivity, with the future goal of a surfactant-free method for the fine control of nanoparticle assembly at air-water interfaces, and subsequent patterning upon deposition.



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Ultrasound-assisted fabrication of red blood cell ghost "bubbles"

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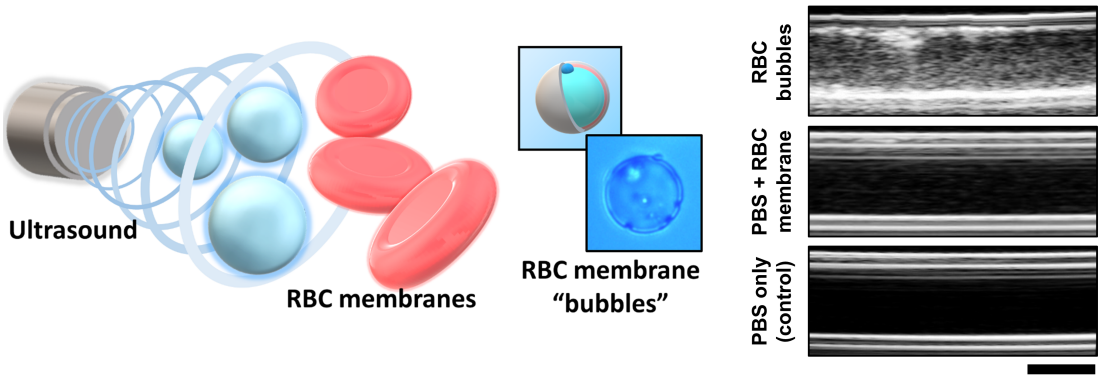
Ultrasound imaging is a non-invasive, relatively inexpensive, real-time, diagnostic imaging technique with a broad application range that can complement other structural and functional imaging modalities. However, this technique is limited by the low contrast between organs or materials with similar "echo-producing" properties, such as blood and tissues surrounding the vasculature, and the poor image quality arising from poorly vascularized tissues, such as tumours or regions with many small vessels with slow blood flow. These cases may require the intravascular application of ultrasound contrast agents, such as gas microbubbles from synthetic lipids and biological proteins, which can effectively reflect sound waves.

Inspired by the inherent biocompatibility and versatility of red blood cell (RBC) or erythrocyte membranes (also known as RBC ghosts), the current work reports an ultrasound-assisted method, utilising human RBC membranes, to produce acoustically active "bubbles", intended for vasculature imaging. The resulting RBC membrane bubbles have an average size of 1.5 μm with a generally spherical morphology, altered internal aqueous compartment contents, and small gas-containing protrusions or "pockets" in between the membrane bilayer. *In vitro* ultrasound imaging showed that RBC membrane bubbles had comparable ultrasound contrast enhancement as the standard DEFINITY™ microbubble preparation (~13% v/v). This current technology demonstrates a new and important application of RBC membranes as ultrasound contrast agents with inherent biocompatibility and the potential for development of new types of ultrasound imaging agents without the use of additional lipid components or pre-made microbubbles.



Engineering Polymeric Nanocapsules with High Aspect Ratio as a High Drug-Payload and Long-circulating Drug Delivery System

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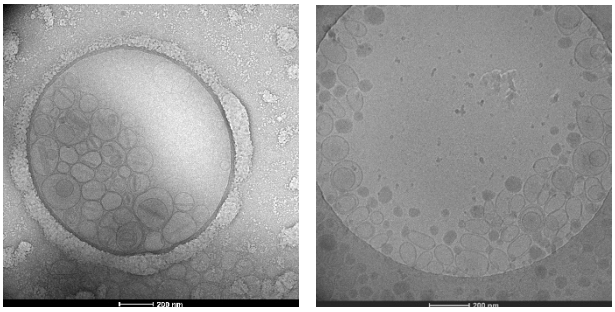
Most nanoparticles used for medical applications suffer from low treatment efficiency and serious side effects due to their short circulation time in the body and burst release. Elongated shape was found to be able to minimize the internalization of nanoparticles by macrophages and hence increase the circulation time[1]. Polymeric material provides a less permeable membrane so drugs were release more slowly. This project thus aims to make use of both features to engineer elongated nanocapsules to increase circulation time and improve controlled release.

Vesicle templating method[2] was adapted, in which elongated liposomes[3] were used as the template and polymers were directed to grow via RAFT polymerization on the surface of the liposomes. The shape and aspect ratio of the nanocapsules prepared after polymerization were characterized by cryo-TEM and small angle neutron scattering (SANS) with BILBY[4]. Lastly, cellular interactions between macrophages and elongated nanocapsules will be compared to their spherical counterparts and their drug release profile will be constructed via ultrafiltration.

Cryo-TEM images showed that elongated liposomes were successfully prepared with encapsulated drug nanocrystals (Figure 1a). With these templates for adsorption of RAFT oligomer, the RAFT polymerization was driven onto the surface of the liposomes. There was no destruction of the interior space for drug encapsulation and the elongated shape of the liposome templates were kept relatively intact (Figure 1b) comparing to some nanocapsules made with spherical templates in the literature[5].



a b

Figure 1 a) Elongated liposomes were successfully prepared with encapsulated drug nanocrystals; b) Elongated shape was maintained in the final polymeric nanocapsules

Elongated nanocapsules were prepared with elongated liposome templates. Further investigation will focus on keeping the drug in nanocrystal form. Cellular interactions and drug release will be investigated to decrease dosage frequency and the side effects.

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Tuning nanostructured lyotropic liquid crystalline mesophases in lipid nanoparticles with protic ionic liquids

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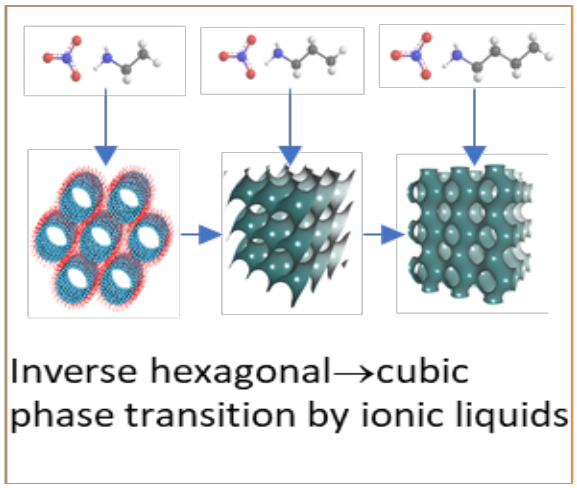
Amphiphile self-assemblies containing highly ordered, mesoporous nanostructures have a wide range of applications in soft templating, drug delivery, catalysis and separation.[1] We herein report 13 protic ionic liquids (PILs) as tunable solvation media to regulate the internal lyotropic liquid crystalline mesophase of monoolein-based nanoparticles. A range of complex nanostructures, including inverse bicontinuous cubic phases (primitive and double diamond), inverse hexagonal phase, and sponge /lamellar phases, were produced and verified by synchrotron small angle X-ray scattering technique (See Figure below). Notably, manipulating the cation/anion structures of the PILs can alter the monoolein packing behaviour and cause a sequential phase transition (hexagonal → cubic → lamellar) in the nanoparticles by decreasing the interfacial curvature of the lipid membrane. The dimension of the hollow pores inside the nanoparticles was also enlarged up to 40% under certain PILs-water solvation systems, making these materials more suitable for encapsulation of large molecules. Finally, a freeze-drying study demonstrated that PILs also possessed the ability to preserve the nanostructures upon reconstitution of the nanoparticles compared to those in pure water. This study opens a new composition range for formulating liquid crystalline materials in PILs-based solvent conditions.



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Branching out: Dynamic interactions of surface decorated nanoparticles at the nano-bio interface

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Effective delivery of therapeutic compounds remains limited by our understanding of interactions between drug carriers at the nano-bio interface. Cationic cell penetrating peptides (CPPs) are reported to enhance the cellular absorption of therapeutic compounds. We anticipate CPP architecture to play a crucial role, but it has not been explored systematically in this context.

We designed CPPs with three distinct architectures to study the influence of CPP structure on cell interactions. Poly(lactic-*co*-glycolic) acid (PLGA) nanoparticles functionalized with CPPs were produced using microfluidics (Fig. 1A). Using single particle tracking we followed the dynamic behaviour of individual CPP-tagged nanoparticles and observed localisation of the nanoparticles in close proximity to the cell membrane (Fig. 1B). After 1 h, branched TAT displayed mobility behaviour distinct from the other peptides with a higher degree of membrane interaction. CPP architecture influenced nanoparticle-cell interactions and provides insights into the drivers that govern cell uptake of nanomedicines.

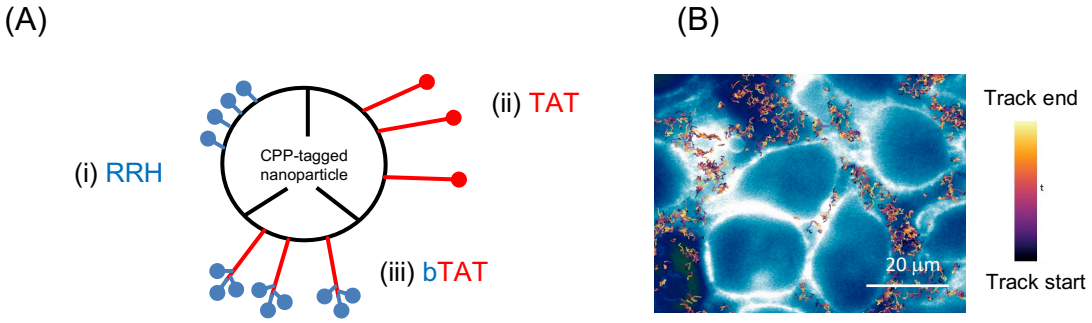

Fig. 1 (A) Schematic diagram of CPP-tagged PLGA nanoparticles. CPPs of different architecture (i) short arginine-arginine-histidine (RRH) (ii) long linear trans-activating transcriptional activator (TAT) (iii) Branched TAT, TAT with three terminal RRH groups (B) Single particle tracking of fluorescently-labelled PLGA nanoparticles during incubation with HeLa cells.

Melbourne – Poster Abstracts

Size-dependent Cellular Internalization of PDA Bowl-shaped Mesoporous Nanoparticles

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A comprehensive study of cellular internalization mechanisms of nanoparticles is crucial in order to optimize their drug delivery efficacy, as endocytosis pathways will likely determine their biological fate. Particularly for polydopamine (PDA) bowl-shaped mesoporous nanoparticles, their anisotropic morphology provides enhanced cellular internalization efficiency with respect to their spherical counterparts.[1]

Herein, we investigated the size-dependent endocytosis pathways of PDA bowl-shaped mesoporous nanoparticles (PDA bowls) in the HeLa cell line. The cellular internalization behavior of PDA bowls was investigated using a set of characterization techniques including flowcytometry, confocal microscopy, and transition electron microscopy. Obtained results demonstrated that the uptake efficiency of PDA bowls is significantly dependent on their size. Moreover, the size of bowls also plays an important role in the endocytosis pathways followed to internalize them into cells, which was investigated by blocking certain endocytosis pathways using inhibitors. Taken together, this work provides fundamental understanding of the impact of PDA bowls diameters on cellular uptake and their endocytosis pathways, which paves the way for the development of drug delivery platforms based on PDA particles with anisotropic morphology and tunable diameter.

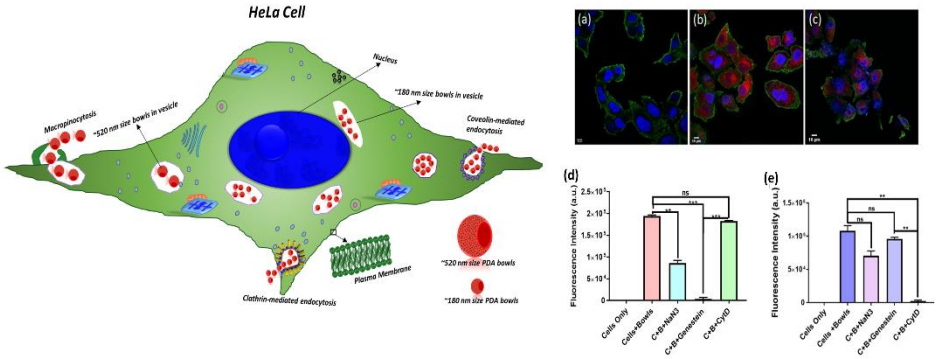

Figure 1. (A) Schematic diagram of size-dependent cellular internalization of PDA bowls. Confocal images (a to c), (a) only cells, (b and c) cells after incubation with ~180 nm and ~520 nm size PDA bowls for 24 h. Fluorescence intensity analysis of inhibitor treated and non treated HeLa cells after incubation with PDA bowls (d) ~180 nm and (e) ~520 nm for 24 h.

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Using the Pair-Angle-Distribution-Function to Analyse Protein Structure.

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X-Ray Free Electron Lasers provide a means of conducting crystallography experiments with remarkable time and spatial resolution. These methods can directly recover the electron density of the materials analysed, however, stringent requirements such as crystal size, low crystal numbers per exposure, and the crystal order can compromise data quality. Membrane proteins, which do not readily crystallise or meet these requirements [1], are particularly interesting to study as they comprise up to 50% of drug targets [2], but less than 10% of the protein structures in the Protein Data Bank [3]. The Pair Angle Distribution Function (PADF) describes the three and four body correlations of the electron density in a sample, and can be recovered from X-ray angular cross-correlation analysis [4]. Although it does not recover the electron density directly, it still contains significant information about the local three dimensional structure of the material. PADF analysis also has the potential to relax the stringent crystal requirements imposed by current XFEL experiments, allowing for multiple microcrystals per exposure within the surrounding solution matrix. We discuss the sensitivity of the PADF to different protein structures [5], and the correlations generated at different length scales; from atomic bonding to tertiary structure. Our aim is to develop PADF analysis to be used complementarily with conventional crystallography analysis, by allowing novel sample preparations of microcrystals suspended in a buffer solution, and to use changing correlations to measure conformational changes in proteins.

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Differences in the self-assembly of lipids in human colostrum and an emulsified colostrum lipid mixture during digestion

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Objectives: Colostrum contains lipids and bioactive proteins that can stimulate the development of organs and prevent diseases in infants.[1] Surprisingly there have been no reports of colostrum being assessed in the context of lipid digestion, which is critical in the transport of lipophilic nutrients. Hence, this project aims to understand the differences in the self-assembly of lipids during the digestion of human colostrum and emulsified colostrum-mimicking lipid mixtures and the potential interactions with bioactive proteins.
Methods: Human colostrum samples were digested under intestinal conditions. The *in vitro* digestion model was coupled to small-angle X-ray scattering at the Australian Synchrotron, enabling acquisition of phase formation as a function of extent of digestion.[2] Emulsified colostrum-mimicking lipid mixtures were formulated by weighing known amounts of triglycerides and dispersing the lipids with a buffer.
Results & Discussion: Prior to digestion, a lamellar phase was present in human colostrum caused by the formation of calcium soaps due to self-digestion by the breast milk's own bile salt-stimulated lipase (BSSL). In contrast, a lamellar phase was not evident in the emulsified colostrum-mimicking lipid mixture before the start of digestion due to the absence of BSSL and only grew once digestion was initiated. However, a cubic phase was observed as digestion progressed for the emulsified mixture, but not human colostrum. *In situ* monitoring of the lipid liquid crystalline structures formed during the digestion of emulsified colostrum mixture revealed additional phases formed due to differences in extent of digestion as compared to human colostrum. Further studies to increase extent of digestion such as including bile salt micelles and consequent interaction with bioactive proteins will elucidate the role of lipid structuring in the overall function of human breast milk.

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High Throughput Quantitative Determination of Protein Solubility and Structure in Ionic Liquids

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Proteins are often utilised for a range of applications in the pharmaceutical, biological, chemical and food industries[1-2]. The ideal solvent for hydrophilic proteins is usually buffered water due to its minimal cost, and ability to mimic the native environment of proteins. However, many proteins are hydrophobic and have poor solubility in water. Because of this, organic solvents have been investigated as alternative solvents for biocatalysis[3] and protein extraction[4], but often have detrimental effects on the protein stability and structure. We propose to use ionic liquids (ILs) as an alternative solvent, or as an additive in aqueous solutions, to control the solubility and stability of proteins. In this project, we will quantify the protein solubility in IL solutions and measure the stability. Initially the model protein lysozyme will be tested in ILs from highly dilute to neat. A novel, high throughput method has been developed to quantitatively determine the solubility of lysozyme. The aim is to explore specific-ion effects and how these differ for concentrated IL solutions compared to conventional dilute salts. A variety of techniques including UV/vis spectroscopy, Fourier-transformation infrared spectroscopy, circular dichroism and small angle x-ray scattering will be used to describe the stability and structure of the protein, and to gain insight into its interactions with ILs. Further studies will extend this work to compare variations in the specific ion effects to other proteins, and to begin building a database of quantified protein solubility and stability in ILs.

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Design and synthesis of an azobenzene-betaine surfactant for photo-rheological fluids

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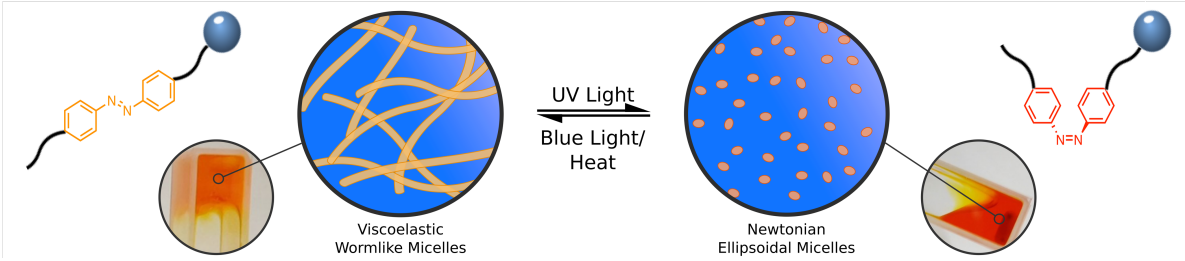
Photo-rheological fluids (PRFs) are materials that modulate their flow properties, such as viscosity and elasticity, when exposed to light of a specific wavelength. The unique stimulus-responsive properties of PRFs, driven by control of nanoscale surfactant aggregates, gives them potential for application in microfluidics, mineral extraction, bioseparations, drag reduction and templated synthesis.[1,2] Most PRFs comprise a mixture of surfactants, additives and salts, in order to elicit the desired stimulus-responsive rheological properties, however, development of more simple, robust and effective systems is a necessity for their broad uptake and integration of such chemistry.[3]

Our work has centred around the development of a novel azobenzene containing surfactant (shown below), capable of forming a PRF without the need for any additives, salts or co-surfactants. Irradiation of the aqueous solution state molecule results in switching of the surfactant aggregates from entangled wormlike micelles to discrete ellipsoidal aggregates, accompanied by concomitant changes in zero-shear viscosity up to 16,000×.

These experiments reveal fundamental and previously unexplored structure-function relationships of azo-surfactants and demonstrate the power of molecular design in realising novel colloidal materials with stimulus-responsive, switchable properties.



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New insights into colloidal phase transitions using neutron scattering techniques

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The fundamentals of crystallisation and glass formation in atomic systems are not yet fully understood. Colloidal nanoparticles have been shown to be promising model systems for understanding crystallisation and glass formation in atomic systems: As colloidal motion is Brownian, rather than ballistic, kinetics and dynamics are orders of magnitude slower than in atomic systems and can be studied in real-time. However, despite previous work, key elements are still missing from our understanding of phase transition in colloidal suspensions especially regarding metastability, supercooling and the glass transition. In particular, there is still no clear understanding of the effects of polydispersity: although studies of both polydisperse and binary mixtures of hard sphere colloids have been performed, a systematic study of the effects of polydispersity on structure, crystallisation kinetics and particle dynamics is still lacking.

One of the reasons for this is the relatively limited types of suspensions which have be studied - most particles used for such studies need to be suspended in mixed solvents for refractive index matching for light scattering studies, which introduces potential problems such as selective solvation and evaporation. In this work we explore the possibility of using ionic liquids (ILs) and deep eutectic solvents (DESs) as the suspending solvent, as these can be tuned to match the refractive index of the particles, and don't suffer from evaporation. We will then develop suitable binary colloidal suspensions consisting of deuterated & non-deuterated nanoparticles suspended in the solvent. With a combination of lab techniques and beam time allocations at the Australian Synchrotron, ANSTO and overseas neutron facilities, we will expansively investigate the nature of metastability, crystallisation and the glass transition, and provide a significant advance on our current understanding of these processes.

Exploring the nanostructure of a deep eutectic solvent at solid interfaces

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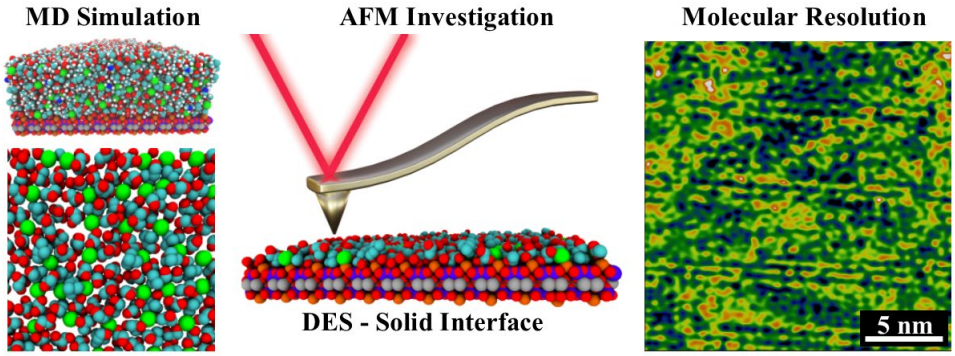
Deep eutectic solvents (DESs) are an attractive class of tuneable solvents for electrochemical systems, materials chemistry, catalytic processes, and chemical extraction.[1,2] To date, the study of deep eutectic solvent nanostructure has largely focused on the bulk liquid, or relied on inferences from surface force analysis. However, accurate understanding of interfacial ordering is vital for industrial applications such as catalysis and electrodeposition, where the structure of the solvent can directly dictate the nature and efficiency of a reaction process.

In order to gain a better understanding of the interfacial behaviour DESs, we employed a combination of high-resolution amplitude-modulated atomic force microscopy and molecular dynamics simulations to elucidate the lateral and near-surface nanostructure of the DES choline chloride:glycerol probed at the mica and highly-ordered pyrolytic graphite interfaces, representing archetypal hydrophilic and hydrophobic surfaces, respectively. Importantly, the adsorbed DES layer in both systems is strongly ordered and reflects a balance between liquid-structure factors and surface templating effects. The surface nanostructures elucidated significantly expand our understanding of the DES interfacial behaviour and will enhance the optimization of DES systems for surface-based applications.



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Investigating virus-host cell interactions in 2D / 3D cell culture models with AFM

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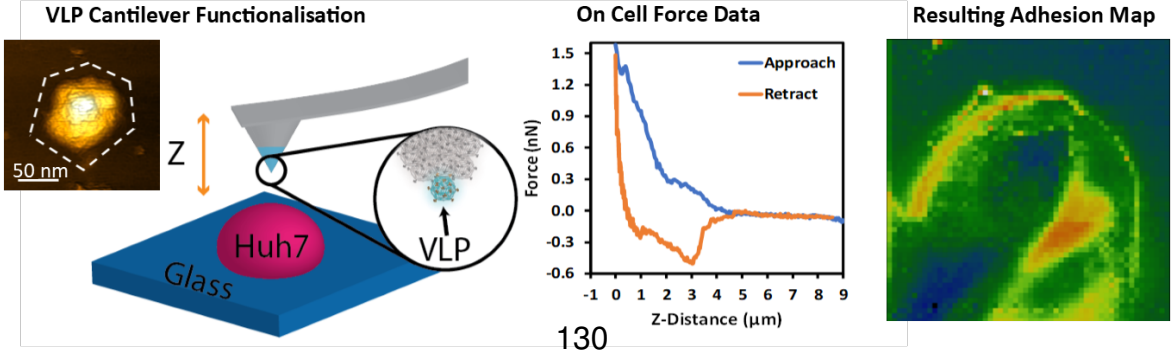
Recent studies are changing the way researchers approach utilizing cell culture systems to address complex research questions. For example, cell cultures have been successfully used to study hepatitis C virus (HCV) for many years. However, most work has been done using traditional, 2-dimensional (2D) cell cultures (cells grown as a monolayer in growth flasks or dishes). Studies have shown that when cells are grown suspended in an extra-cellular-matrix-like material, they develop into spherical, 'organoid' arrangements of cells (3D growth) that display distinct differences in morphological and functional characteristics compared to 2D cell cultures. In liver organoids, one key difference is the development of clearly differentiated apical and basolateral surfaces separated and maintained by cellular tight junctions. This phenomenon, termed polarity, is vital to normal barrier function of hepatocytes in vivo. It has also been shown that viruses, and virus-like particles, interact very differently with cells derived from 2D as compared to 3D cell cultures, bringing in to question the usefulness of 2D cell cultures to study virus-host cell interactions. Here, we investigate differences in cellular architecture as a function of cell culture system, using confocal scanning laser microscopy, and determine differences in binding interactions between HCV virus-like particles (VLPs) and their cognate receptors in the different cell culture systems using atomic force microscopy (AFM). We generated organoid cultures that were polarized, as determined by localization of key apical and basolateral markers. We found that, while uptake of HCV VLPs by both 2D and 3D Huh7 cells was observed by flow cytometry, binding interactions between HCV VLPs and cells were measurable by AFM only on polarized cells. The work presented here adds to the growing body of research suggesting that polarized cell systems are more suitable for the study of virus infection and dynamics than non-polarized systems.



Delivery of antimicrobial peptides to model membranes by cubosome nanocarriers

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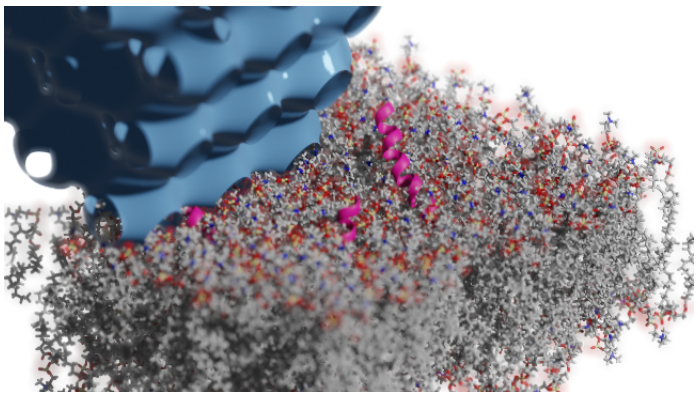
Antimicrobial peptides (AMPs), which typically disrupt the bacterial wall prompting leakage or lysis of the cell, form a growing contingent in the arsenal against antibiotic resistant bacteria. The effectiveness of AMPs is, however, hampered by their low solubility, general chemical and physical instability, and short half-life in vivo. Lipid nanocarriers such as cubosomes are effective at encapsulating and protecting proteins while simultaneously showing promise in delivery applications. Here, the efficacy of cubosome mediated delivery of AMPs is evaluated by the in-situ surface characterization of model membranes with varying composition. The cubosomes were observed to initially fuse with the membranes, with subsequent membrane disruption observed after approximately 20 – 60 min. The time for the disruption was sensitive to the charge of the cubosome as well as the composition of the bilayer. More physiologically relevant bilayers including lipids with phospho-(1'-rac-glycerol) (PG) or phosphoethanolamine (PE) headgroups were more vulnerable than those of neat phosphocholine (PC). Notably, disruption to the bilayer occurred an order of magnitude faster for encapsulated AMP compared to free AMP.



Effect of fat content on the solubilization of halofantrine in infant formula during in vitro digestion

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Low drug solubility is a major obstacle to the absorption of drugs from gastro-intestinal tract. One strategy to improve the oral absorption of poorly water-soluble drugs is to co-administer them with lipids. Lipid digestion products interact with endogenous bile salts and phospholipids in the small intestine to form a solubilising environment for poorly water-soluble drugs. Our group has previously demonstrated that infant formula is a suitable source of lipids to enhance the solubilisation of the poorly water-soluble drug halofantrine during in vitro intestinal digestion [1]. This study investigated the effect of changing the amount of fat present during the digestion of infant formula on the solubilisation of co-administered halofantrine. A supersaturated quantity of halofantrine was mixed with reconstituted infant formula containing 3.8%, 1.9% and 0.95% fat to produce a halofantrine suspension. Each halofantrine suspension was digested with porcine pancreatin in vitro and the solubilisation of halofantrine was monitored using in situ small-angle x-ray scattering. It was found that the halofantrine was almost completely solubilised during digestion at each of the fat concentrations tested. The rate of halofantrine solubilization increased as the fat content of the formula increased.

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Formulation and characterization of lyotropic liquid crystalline lipid nanoparticles in designer ionic solvents

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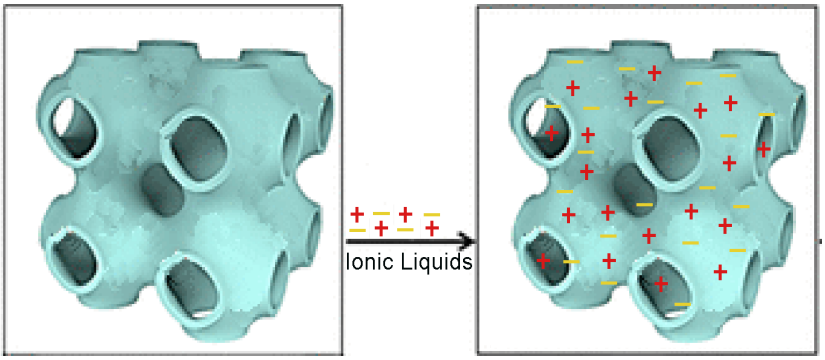
Lipid-based cubosomes are the submicron nanoparticle dispersions of the lyotropic liquid crystalline cubic phase. These particles have been shown to be excellent drug nanocarriers candidates. However, some limitations remain which are related to the production of cubosomes including their low stability, and their small water channel size for the encapsulation of biomolecules. Herein, we propose using biocompatible amino acid ionic liquids as formulation components to address these limitations. We hypothesis that the amino acid ionic liquids will have the ability to modify the structure and physiochemical properties (such as surface charge, pore size, stability, drug encapsulation) of the cubosomes, and support the design and engineering of cubosomes suitable for drug delivery, with a focus on gene therapy. Small angle X ray scattering (SAXS), dynamic light scattering (DLS), and cryogenic electron microscopy (Cryo-TEM) will be used to examine the microstructure and physiochemical properties of the cubosomes. I will present our experimental design and hypothesis with preliminary results at the conference.



The effect of salt and particle concentration on the dynamic self-assembly of detonation nanodiamonds in water

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Nanodiamonds have unique physiochemical properties that are exploited in many applications from drug delivery and biosensing to composite materials and abrasives[1]. Detonation nanodiamonds are colloidally stable in water, but dynamically self-assemble into complex, fractal-like structures. While this interesting colloidal behaviour has been reported by our group[2] and others[3], the underlying mechanisms remain poorly understood and most investigations to date have focused on electron microscopy-based studies.

We report the effect of salt and particle concentration on the dynamic self-assembly of ~ 5nm detonation nanodiamonds suspended in water. We employ dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) to demonstrate that the self-assembled structures are present in suspension and not only in electron microscopy experiments on solid substrates or vitrified water. We demonstrate that the self-assembly process depends on the concentration of particles in suspension and that it is largely independent of the salt concentration. Our results suggest that the complex chemistry and charge distribution on nanodiamond surfaces leads to a unique form of dynamic aggregation and self-assembly in solution, paving the way towards an improved understanding of their colloidal properties, with the potential for novel applications.

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Optimal quantum dot size for sensitizing photovoltaics with fusion

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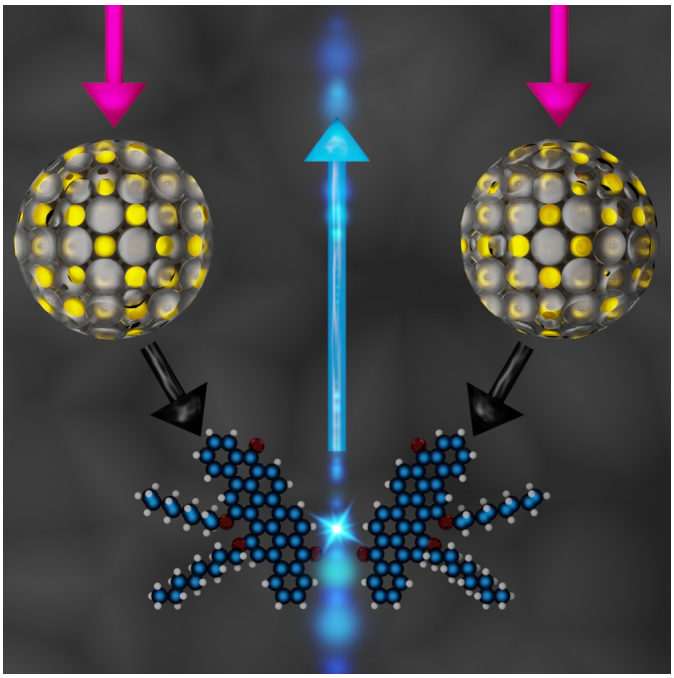
Light fusion increases the efficiency of solar cells by converting photons with lower energy than the bandgap into higher energy photons. The solar cell converts the product photons to current. We use Monte Carlo simulation[2,3] to predict that lead sulfide quantum dot[4] sensitizers will enable fusion with a figure of merit on the mA/cm^2 scale, exceeding current records, while enabling silicon cell compatibility.[1] Performance is highly sensitive to quantum dot size, on the order of mA/cm^2/nm.



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Understanding the behaviour of azobenzene-based, soft matter systems: from molecular design to switching upon confinement

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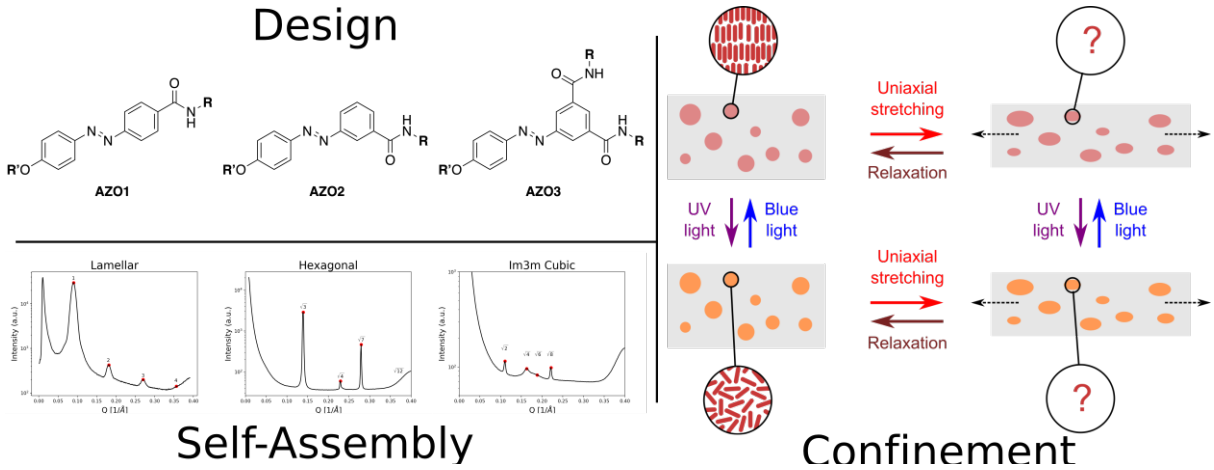
The azobenzene functional group is known to have a facile and reversible photo-induced *E/Z* isomerization. By incorporating this functional group into molecules, materials that exhibit light-induced changes in their chemical or physical functionality can be fabricated. One group of materials of particular interest are condensed matter systems including liquid crystals, photosurfactants and polymeric materials. However, condensed systems can display emergent behaviour such as self-assembly, excimer formation, and surface interactions. It is therefore important to observe and understand these behaviours of azobenzene-based, soft matter systems across a range of length scales and their consequences, including structure-functions relationships for effective molecular design, effects of excimer formation of *E/Z* isomerization, and action of azobenzene-based systems upon confinement at surfaces or 3D defined domains.

Our work explores a range of these interactions across different length scales. Molecular design principles are understood through self-assembly of a library of simple azobenzene building-blocks in binary (azobenzene + solvent) lyotropic liquid crystal systems.[1] Additionally, effects of confinement on liquid crystalline order are explored through the action of azobenzene-doped thermotropic liquid crystals at liquid interfaces and confined in deformable elastomeric matrices.



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Specific Ionic Liquid Effect of Lysozyme Revealed by X-ray Crystallography

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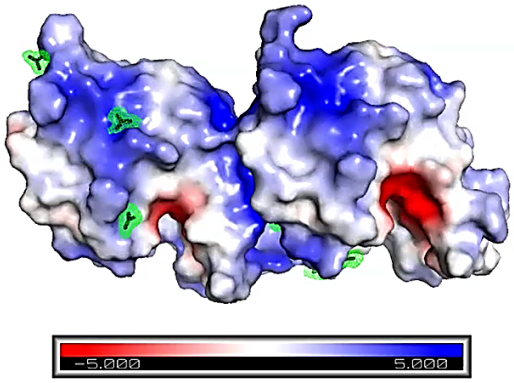
Ionic liquids (ILs) are liquids that are comprised entirely of ions[1]. IL solutions have been widely studied for biochemical applications in recent decades. IL ions interact with proteins, and can profoundly regulate their properties and functionalities. However, it is challenging to gain an in-depth understanding on the specific ion-protein interactions at the molecular level[2]. In addition, the specific ion effect of ILs on protein stabilization continues to be a question. Here, we use X-ray crystallography of the model protein lysozyme in a range of ILs, identifying the exact locations and interactions of IL ions with amino acids in lysozyme and the hydration layer. The protein functionalities such as conformational changes, specific interactions, surface charges and compactness with different ions will be discussed. In particular, we show the protein aggregation and crystallization in numerous IL-water mixtures, IL-protein interfaces and interactions at an atomic level. This study can improve our understanding of how and why proteins misfold and aggregate, and specific ion effects for future solvent design for proteins.

Surface charge representation of two lysozyme structures in ethylammonium nitrate, where the red and blue colors correspond to negative and positive electrostatic potentials, respectively, and nitrate ions and the corresponding electron density are shown in green.



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Drying Fronts in Blood Droplets

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The coffee ring effect and other patterns are commonly observed in dried deposits of particle suspensions. These patterns have been proposed as a visualisation method for low-cost diagnostics as deposits vary between patients afflicted with several medical conditions. There has been significant study on pattern formation in simple particle and polymer systems. However, the dominant processes in whole blood are unclear.

A comparison between simple particle and red blood cell suspensions shows significant differences in both final appearance and dynamics. This is caused by variations in cell shape and deformability as well as a significant protein content that effect packing/gelling behaviour. Through drying experiments with cell suspensions and comparison with theoretical work we have identified the dominant processes governing pattern formation in drying droplets of red blood cell suspensions (Figure 1).

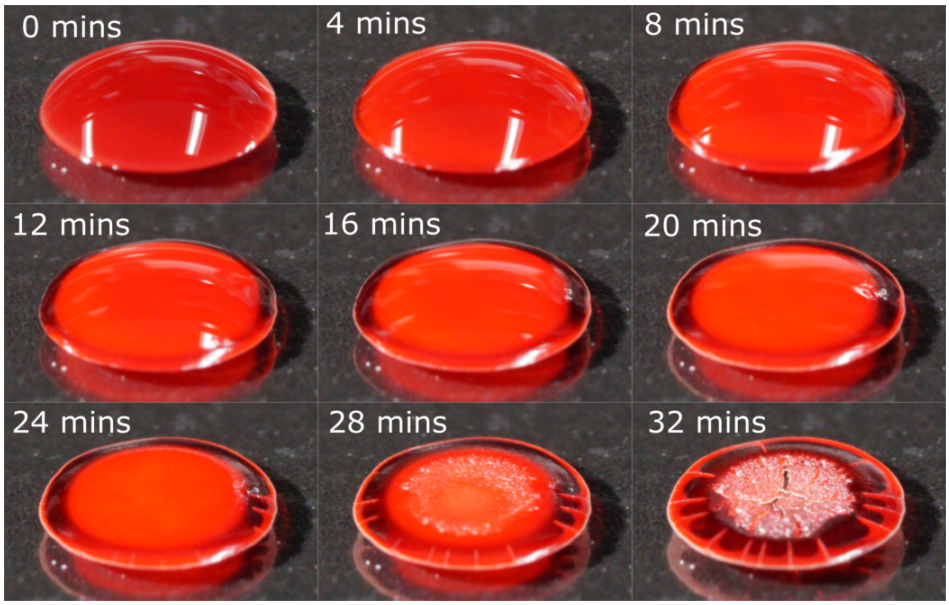

Figure 1. Whole blood from a healthy donor drying on microscope glass

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Drug Resistant Pathogens are Susceptible to Silver Coated Nanotextured Titanium Surfaces

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Antimicrobial resistance is a silent pandemic sweeping the globe. For the past 100 years, antibiotics have prevented infections and diseases caused by fungal and bacterial species. However, it has come to a point where microbes have become multi-drug resistant, adapting and mutating in order to become insusceptible to these drugs. These mutations include an increase in membrane thickness, preventing drug permeability, and physical changes, causing the drugs to not be able to identify the target molecules. We are currently at a crossroad wherein development of new and innovative drugs has decreased in tandem with an increase in antimicrobial resistance. This is where advancements in non-drug related treatments are required.

In this study, multiple hydrothermally etched titanium surfaces were synthesised to mimic the natural antimicrobial nanofeatures found on organisms. These nanostructured surfaces were utilised to investigate the interactions between a change in surface geometry and a decrease in microbial viability. Biological tests using *Methicillin-resistant Staphylococcus aureus* and *Candida auris* were tested on these surfaces, and relatively high antimicrobial activity was noted when compared to control titanium surfaces. However, minimal differentiation of the antimicrobial activity was observed between the textured surfaces of different aspect ratios, meaning that nano-structuring alone was not viable for optimisation of the biocidal action. Further enhancement was carried out via the deposition of a silver thin film atop the nanostructures and the now coated structures provided a secondary mechanism for microbiocidal effects and significantly increased cell death on the surface. This development aids in the advancement of multifaceted, microbiocidal, medical grade, titanium surfaces.

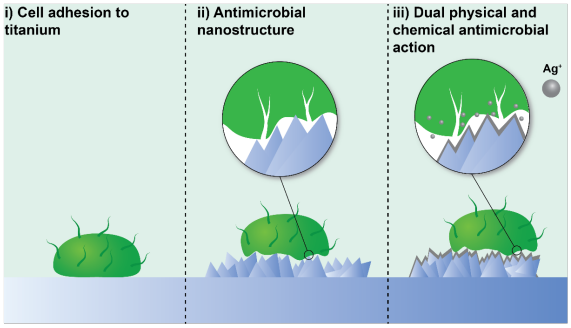

Figure 1. Schematic illustrating the i) normative cell adhesion to a titanium surface, ii) physico-mechanical puncture of microbial cells on a nanotextured surface, iii) a dual physical and chemical mode of antimicrobial action.

Modification of direct ink written dehydrofluorinated poly(vinylidene difluoride) membranes using thiol-based click chemistry

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The alarming rise in scarcity of fresh and safe drinking water around the world has prompted an increase in search for new materials to fabricate more efficient water filtration membranes.[1] Poly(vinylidene difluoride) (PVDF) is a popular membrane material however its use as long lasting membranes is hindered by inorganic fouling, biofouling and compaction. To solve some of these issues, we report on the bulk synthesis of dehydrofluorinated PVDF (dPVDF) which results in alkene moieties along the backbone of the polymer chain, as confirmed by attenuated total reflection – Fourier transform infrared (ATR - FTIR) spectroscopy and Raman spectroscopy.

The dPVDF (with and without a pore forming agent, poly(pyrrolidone) (PVP)) was then fabricated into a dPVDF microfiltration (MF) membrane using a superior deposition technique (direct ink writing (DIW)) followed by non-solvent induced phase separation (NIPS) to produce a porous membrane. The fabricated dPVDF membranes were more hydrophobic (water contact angle (WCA ≈ 115°) than the PVDF membranes (WCA ≈ 99°), yet had greater equilibrium water content (EWC) and porosity (ε), which correlated to the morphology of the fabricated membranes. Importantly, the dPVDF membranes with 30 wt% of PVP (relative to dPVDF concentration) had a pure water flux (PWF) of ~4300 L m^{-2} h^{-1}, which was within the range of commercially available PVDF membranes (~ 6300 – 8100 L m^{-2} h^{-1}).

The advantage of these membranes was further highlighted by the successful modification of the pendant alkene moieties. A thiol having benzoic acid termination was covalently coupled through Thiol-Michael addition click chemistry. The reaction success was monitored by sulphur mapping on the surface and the cross-section of the modified membranes, using energy dispersive X-ray analysis (EDX) scanning electron microscopy (SEM). The pure water flux increased as a result of the membrane modification by hydrophilic carboxyl groups. Additionally, initial trials demonstrated pH responsive behaviour of the modified membranes in the presence of metallic cations. The thiol-Michael addition exhibits tremendous potential for the development of efficient separation membranes capable of detecting heavy metals.

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Effect of surfactant ionicity on critical micelle concentration in aqueous ionic liquid mixtures

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Protic ionic liquids are the largest known solvent class capable of promoting surfactant self-assembly. However, ILs are increasingly used as mixtures with molecular solvents, such as water, to reduce their cost, viscosity and melting point, and the self-assembly promoting properties of these mixtures are largely unknown. Here we investigated the critical micelle concentration (CMC) of ionic and non-ionic amphiphiles in ethylammonium nitrate (EAN)-water mixtures to gain insight into the role of solvent species, and effect of solvent ionicity on the self-assembly process. The amphiphiles used were the cationic cetyltrimethylammonium bromide (CTAB), anionic sodium octanoate sulfate (SOS), and the non-ionic surfactant tetraethylene glycol monododecyl ether (C12E4). Surface tensiometry was used to obtain the CMCs and free energy parameters of micelle formation, and Small angle x-ray scattering (SAXS) was used to characterise the micelle shape and size.

The EAN-water solvents displayed self-assembly results consistent with a salt in water for EAN proportions below 5 mol% across all three surfactants, leading to CMC values lower than the CMC observed in water. A steep incline in the CMC was observed for concentrations between 5 mol% to 50 mol% of EAN for SOS and C12E4. However, CTAB displayed more complex behaviour where the CMC remained below the CMC of water until 33 mol% EAN. Across all surfactants, a plateau in CMC values were observed at very high EAN concentrations, which could indicate that there is a shift in the dominant solvent beyond EAN concentrations of 50 mol%. This study furthers our understanding of PIL solvent behaviour in ternary mixtures with amphiphiles.

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Monitoring the Adsorption of Ultra-Small Gold Nanoparticles to Model Bio-Membranes.

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Nanomaterials - materials with nanoscale dimensions - are widely used in biological applications, including drug delivery, nanomedicines, emerging antimicrobials, disease diagnostics, cellular-imaging, and tumour (cancer) treatment, amongst many others. In general, nanoparticle-based technologies must interact with, and often cross, a cellular membrane to be utilised. However, the precise mechanism by which nanomaterials interact with cell membranes is poorly understood. This work further develops our fundamental knowledge of the physicochemical, nanomechanical, and structural interactions of gold nanoparticles (AuNPs) at a model DOPC bio-membrane. Specifically, the adsorptive mechanism of action of 5nm AuNP onto a supported DOPC bilayer – a model biomembrane – was observed in real time. Dual AFM and molecular dynamics simulations were used to interrogate the system. AFM experiments elucidated that the AuNP would spontaneously embed into the model bio-membrane and slowly diffuse through the upper leaflet of the lipid bilayer. Verification of the AuNP-SLB interaction was undertaken via MD simulations and revealed, significant reductions in lipid density upon AuNP introduction, as well as significant structural changes of between the mica surface, the DOPC membrane, and the AuNP. More holistically, it was shown that bilayer self-assembly upon a mica surface was feasible using an atomistic MD model and could characterise its interactions with a AuNP.

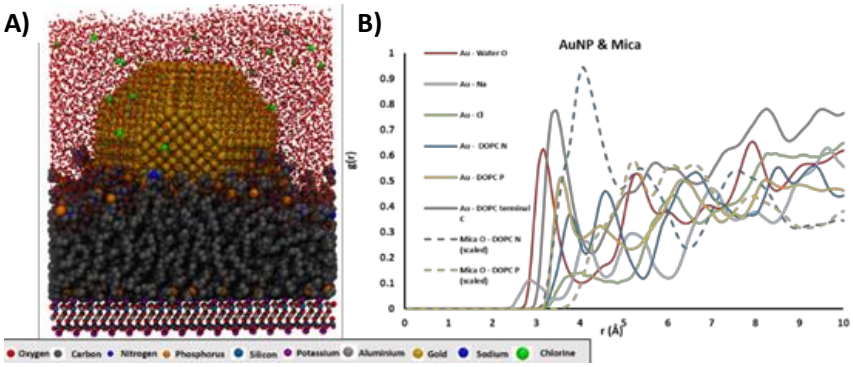

Figure 1. Molecular dynamics simulations of 5 nm Au Nanoparticle adsorption to a DOPC lipid bilayer formed at a mica surface. A) Simulation snapshot. B) Radial distribution data.

Influence of electrolytes on the coalescence of free droplet collisions

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The droplet-droplet collisions play a prominent role in determining the performance efficiency of several mass transfer operations applied in chemical and petroleum process industries. Droplet coalescence is governed mainly by fluid dynamic aspects such as the angle of impact, droplet size distribution, impact velocity, shape deformation, and thin-film drainage which can influence the rates of mass transfer in a process[1]. Film drainage process[2-3] is regulated by the hydrodynamics of liquid film and the interfacial properties of the drops where the influence of surfactant and electrolytes can alter the surface chemistry and the outcome of drop collision. Currently, there exist no model or experimental studies on determining the effect of the surfactants and electrolytes over the coalescence phenomena in realistic free droplet collisions.

In this present work, we have developed a novel method capable to perform collision of freely moving droplets and determine the influence of interfacial properties on droplet coalescence. We acquire a wide extent of coalescence maps and list the outcome of collision by varying parameters such as concentrations, contact time, drop diameter ratio, Weber numbers, and impact velocities which aids to validate a simulated model. The goal of this study is to enable a clear and systematic approach to investigate the effect of surface chemistry on droplet coalescence by conducting collision of freely moving droplets with different electrolytes at high weber numbers imitating the industrial scenarios in most liquid-liquid process systems.

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Environmentally friendly zwitterionic surfactants: synthesis and self-assembly exploration of novel amino acid and betaine surfactants

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Amino acids (one of nature's fundamental building blocks) are well suited as surfactant constituents, due to attractive features such as enhanced biodegradability, biocompatibility as well as their development from environmentally friendly sources.[1] The chief benefit is that there are multiple functional groups available, which can be charged or functionalized as desired.[2] Furthermore, the presence of such functional groups allows metals to complex neatly within the molecule.[3]

We have examined the production of ecologically sustainable chemicals and materials by utilising natural sources to develop novel surfactants. This includes synthesis of new molecules, characterisation, and assessment of their physical properties to determine their potential in various applications. It is well known that amino acid surfactants, and amidopropyl betaines have desirable surface-active properties and are mild on skin, we postulate that libraries of similar molecules will be well suited for personal care products. We seek to develop more information regarding this special class of zwitterionic surfactants, and by creating a library, seek to illustrate their superior properties and potential.

Our previous studies have illustrated that betaine surfactants have exciting, novel and unique viscoelastic properties,[4] and we now seek to investigate the efficacy of new sustainably derived surfactants. We propose the combination of amino acids with different alkyl chains would likely produce biocompatible, readily biodegradable and novel surfactants with a range of beneficial physical properties.

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Modulating Transparency and Colour of Cellulose Nanocrystal Composite Films by varying polymer Molecular weight

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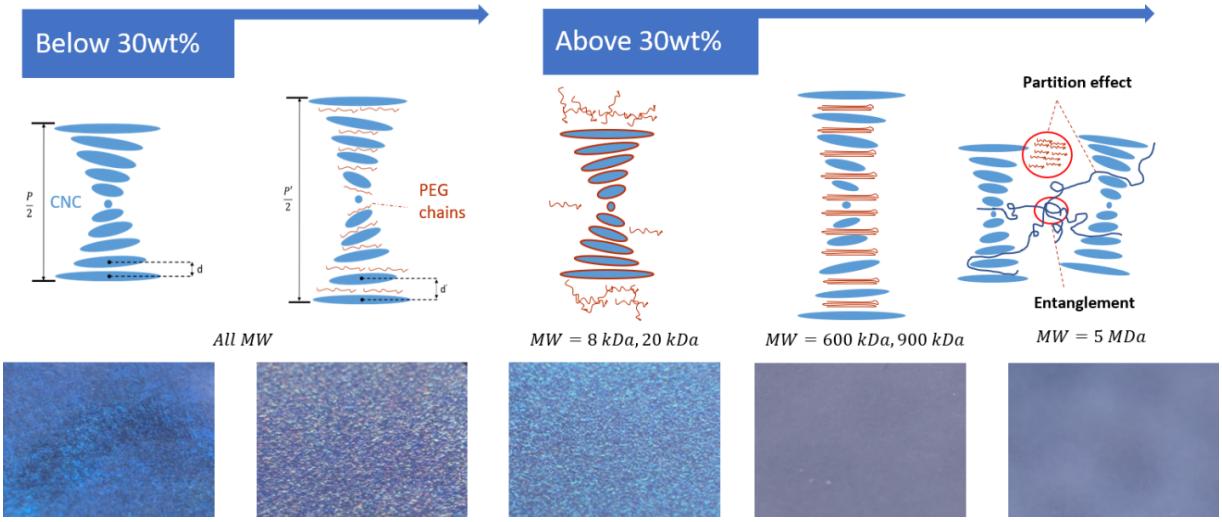
Cellulose nanocrystals (CNC) can produce photonic composite films that selectively reflect light based on their periodic cholesteric structure. Flexible free-standing composite films of CNC incorporating poly(ethylene glycol) (PEG) of five different molecular weights were prepared and characterised by reflectance UV-vis spectrometer, atomic force microscopy (AFM) and scanning electron microscopy (SEM). Films with each molecular weight were investigated over a concentration range. The colour and transparency of the composite films was modified by varying both the PEG molecular weight and concentration. Depending on the molecular weight, the films were able to reflect light from the UV region (252 nm) across the visible spectrum to the infrared region (832 nm). Different trends in variation of the reflected light based on the molecular weight was found with increasing PEG concentration and was explained by weak depletion interactions occurring between CNC and PEG, which was reduced with increasing PEG molecular weight. This research demonstrates the possibility that photonic properties of CNC composite film can be designed by manipulating the PEG molecular weight.



Bioinspired polynorepinephrine and its applications as an efficient drug delivery vehicle and antifouling coating material

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An innovative drug delivery vehicle based on polynorepinephrine (PNE) with controllable size, high delivery efficacy and low cytotoxicity is presented. Highly monodisperse PNE nanoparticles were fabricated by the autoxidation of norepinephrine monomers in an alkaline water/ethanol mixture via stirring at room temperature. We demonstrated the facile optimization of particle size to enhance particle stability and biocompatibility by varying solvent and monomer dosage. To demonstrate the suitability and potential application of PNE particles in cancer therapy, we showed that these particles were biocompatible *in vitro* with HeLa cells and *in vivo* in zebrafish embryos. After loading the anti-cancer chemotherapy drug doxorubicin (DOX) into the PNE nanoparticles, a consistent and pH responsive drug release profile of DOX was achieved in different environmental conditions. It was found that DOX loaded PNE nanoparticles (PNE/DOX) exhibited much higher pharmaceutical cytotoxicity than free DOX on HeLa cells, and that DOX was selectively released within extracellular tumour mimic microenvironments (pH 5.0).[1]

PNE is also a promising coating material. We found that PNE coatings showed superior protein resistance against a model biofoulant (bovine serum albumin, BSA) when compared with polyethylene glycol (PEG) and polydopamine (PDA) coatings. The antifouling mechanism between BSA protein molecules and coating films was investigated using atomic force microscopy (AFM). We also demonstrated that PNE modified surfaces presented remarkable bacterial killing ability against both Gram-positive Staphylococcus aureus (S. aureus) and Gram-negative Escherichia coli (E. coli) bacteria after being irradiated with 850 nm near-infrared (NIR) laser light. [2]

Taken together, PNE represent a new class of melanin materials with promising potential in various applications including drug delivery, surface modification, bacterial control, and so on.

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Phenolic ester-decorated cellulose nanocrystals as anti-UV reinforcement nanofillers in polyvinyl alcohol films

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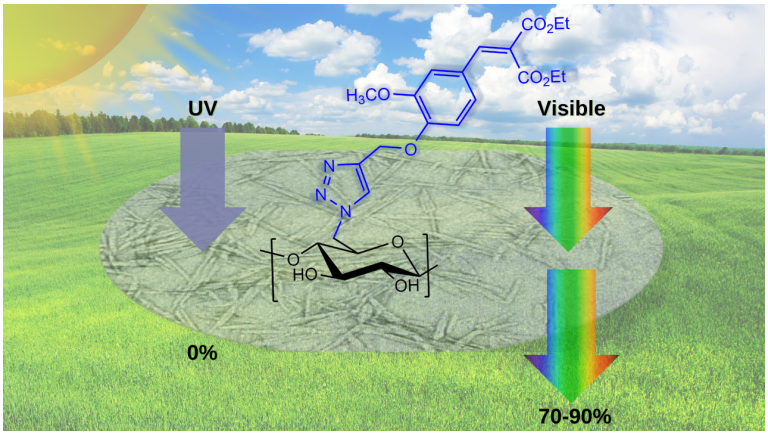
Grafting novel and nature-inspired phenolic esters onto cellulose nanocrystals (CNCs) can provide excellent protection against UV radiation[1]. Here, we decorate cellulose nanocrystals with a UV-absorbing phenolic diester (diethyl ferulate [DEF]) *via* click-type copper-catalysed azide/alkyne cycloaddition (CuAAC) reaction. When the decorated CNCs (CNC-DEF) were incorporated into polyvinyl alcohol (PVA) matrix, transparent films with excellent photostability and UV-absorbing properties were achieved. PVA films loaded with 20 wt% CNC-DEF exhibit complete UVA and UVB protection (0% transmittance) and high transparency in the visible region (70-90% transmittance). On the contrary, PVA films loaded with pristine CNCs do not exhibit UV shielding properties. Results also revealed that grafting DEF on CNCs aids with the dispersion of the phenolic diester in the aqueous PVA matrix. Mechanical tests also show that the addition of 20 wt% CNC-DEF in PVA increases the tensile strength and modulus by 88% and 150%, respectively, relative to neat PVA. This study shows the potential of the phenolic-ester decorated CNCs as multifunctional UV-absorbing reinforcement fillers in PVA films for industrial and packaging applications.



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Development of pH-responsive Hexosomes and Cubosomes using novel ionisable Aminolipids

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Lyotropic liquid crystalline (LLC) lipid nanoparticles have gained attention as drug delivery systems due to their ability to carry a wide range of hydrophobic and hydrophilic drugs. Among others, cubosomes, with an internal bicontinuous cubic (Q_2) structure, show fast drug release and more vital membrane interaction, in contrary, hexosomes (H_2) exhibit much slower release profile (Figure 1)[1].
In this study, we synthesised nine novel ionisable Aminolipids with tertiary amine-containing headgroup and formulated them in Monoolein (MO) / Pluronic based dispersions. We hypothesise that at physiological pH (7.4), the lipid headgroup charge is neutral, and the nanoparticles exhibit characteristics of slow release phases such as H_2. At lower pH (5.0-6.5), the headgroup is protonated with a positive charge, which drives the system to Q_2 phase for faster drug release and stronger fusion with cancer cell membranes (Figure 2).

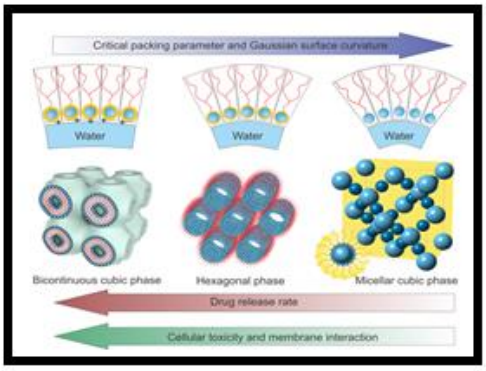

Figure1: Non-lamellar LLC phases and their properties

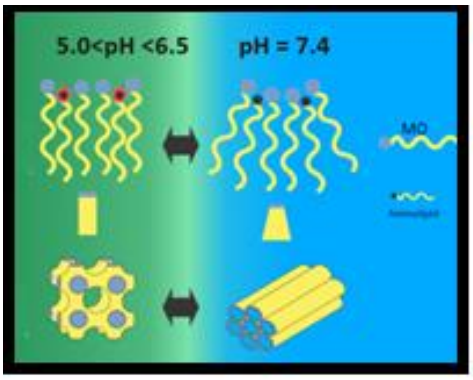

Figure2: Aminolipid incorporation to MO nanoparticles

Using high throughput formulation and synchrotron small angle X-ray scattering (SAXS), the effects of aminolipid structure and concentration on the mesophase of MO nanoparticles at various pHs were determined. As the pH changed from neutral to acidic, mesophases were formed in an order L_2 (inverse micelles) → H_2 → Q_2. Specifically, systems with heterocyclic oleates exhibited the H_2 to Q_2 transition at pH 5.5-6.5. Furthermore, the phase transition pH can be fine-tuned by incorporating two aminolipids into the nanoparticles. Nanoparticles with a pH-dependent phase transition as described in this study can be useful as drug delivery carriers for the treatment of cancers and specific bacterial infection.

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Polymer-silica core-shell capsules for versatile copper extraction

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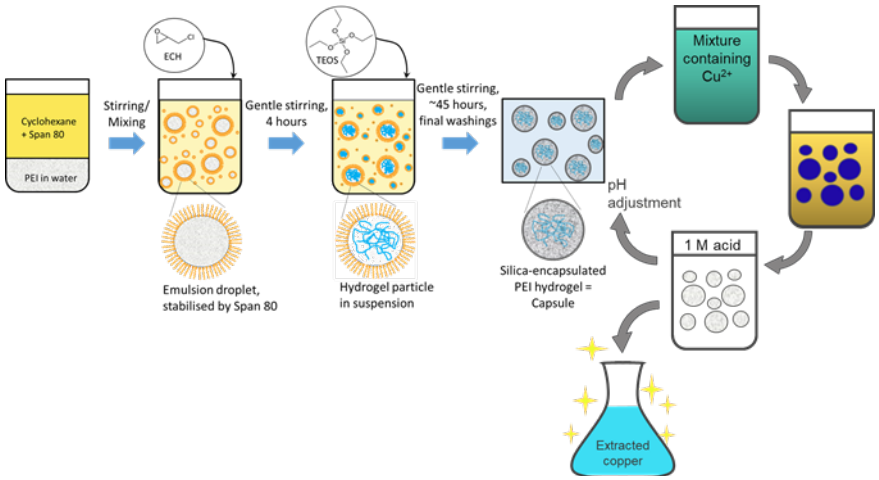
The depletion of natural resources together with growing contamination problems cause a pressing demand for efficient refining/purifying methods and materials. For instance, the growing limitation of copper stocks concurrent with increased copper pollution motivate the search for alternative methods of copper extraction and retrieval from acidic, complex, multiphase media.

In this study, employing a simple one-pot synthesis method,[1] polyethylenimine (PEI)/SiO_2 core–shell capsules were developed that act as highly efficient binding agents for copper, even in acidic conditions that are relevant to most cases corresponding to copper extraction. At the same time, the especially smooth surface of the silica shell provides a robust, inert protective coating, allowing use of these capsules in multiphase mixtures, such as concentrated sludges, mine tailings, soils and comminuted ores. The results demonstrate that capsules can be fully recycled to their original state by simple washing with 1 M acid, and thereby can be repeatedly used for copper extraction without loss of efficiency. The efficient synthesis, and extraction/recycling open up new opportunities for refining/purifying technologies in various sectors of industry.

Synthesis of capsules and their use in copper extraction cycle.



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Exploiting imperfections in few-layer black phosphorus for a broad-spectrum antimicrobial

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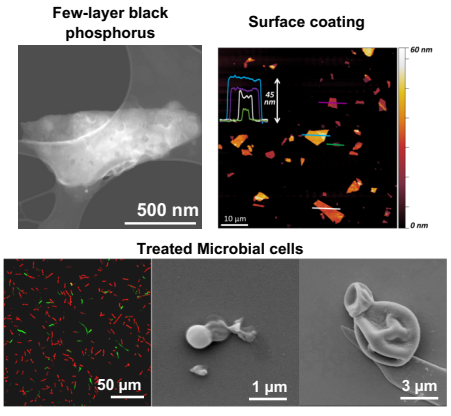
Antimicrobial resistance (AMR) has rendered many conventional therapeutic measures, such as antibiotics, ineffective. This makes the treatment of infections from pathogenic micro-organisms a major growing health, social and economic challenge. Recently, nanomaterials, including two-dimensional (2D) materials, have attracted scientific interest as potential antimicrobial agents. Many of these studies, however, rely on the input of activation energy, and lack real-world utility. In this work, we present the broad-spectrum antimicrobial activity of few-layered black phosphorus (BP) at nanogram concentrations. This property arises from the unique ability of layered BP to produce reactive oxygen species (ROS) which we harness to create this unique functionality. BP is shown to be highly antimicrobial to-wards susceptible and resistant bacteria and fungal species. To establish cytotoxicity with mammalian cells, we specifically show that L929 mouse fibroblasts were metabolically unaffected by the presence of BP. Finally, we demonstrate practical utility of this approach, whereby medically relevant surfaces are imparted with antimicrobial properties via functionalization with few-layer BP. Given the self-degrading properties of BP, this study demonstrates a viable and practical pathway for the deployment of novel low-dimensional mate-rials as antimicrobial agents without compromising the composition or nature of the coated substrate.



3D Printing Microfluidic Devices to Study Adhesion between PS coated Droplets

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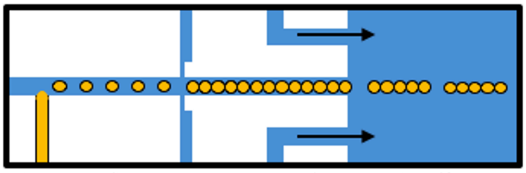
The application of 3D-printing technology to fabricate microfluidic devices with sub millimetre channel dimensions has evolved as the 3D printer resolution has improved overtime. Compared to conventional fabrication process (e.g. photolithography and soft lithography) that can be time-consuming and costly, 3D-printing techniques allow for more faster and cheaper iterations of the design. However, as a new rapidly evolving technology, 3D-printing also has limitations including resolution, surface roughness, surface wettability, transparency and difficulty in removing support materials. In this work, we have explored a number of 3D printer technologies to print transparent devices with print resolutions as small as $60\mu m$. Due to challenges in removing support material inside the channels in sealed devices, we have adapted our design iteration methods to print the device in an open-channel configuration and glue it onto a glass slide using an adhesive bonding method[1]. This method takes advantage of the capillary force between the two bonded substrates to deliver the UV curable glue.

The fabricated devices are used for probing adhesive forces between oil droplets that are coated with polymer/surfactant (PS) complexes in a high throughput context. Building on previous designs developed in our group[2], we have developed a new design as seen from the schematic of the device shown in the figure below. The device has three sections for drop generation, drop collision and forming drop chains, respectively. The design is being iterated to optimise for polymer-surfactant systems that are expected to see drop chain formation. Initial measurements indicate that these devices can in fact generate drop chains based on adhesion. Additionally, these data have identified design changes to the drop pathway to control adsorption time and dilution.



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Understanding Polymer silica core shell micro composites

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The complexity of polymer encapsulation is essential owing to the wide applicability of the technique. Persistent pollutants such as perfluoroalkyl substances and active pharmaceutical ingredients (APIs) found in the soil and water matrix require specially designed molecules that concentrate them and aid in their reuse or destruction. The existing treatment technologies are non-specific and economically inefficient due to transport of matrix and the amount of solvent used. Polymeric adsorbent with ability to adsorb these moieties are sought after and encapsulated polymers can prove to be efficient for remediation of complex matrices. Strategies have been developed to encapsulate different polymers. This work incorporates a combination of emulsion and interfacial polymerisation[1] that yields polymer silica shells displaying unique chemical and physical properties. The use of branched polymers like Polyethyleneimine (PEI) also results in cost effective synthesis of polymer core and makes the capsules customisable for different applications. The chemistry of PEI supports the formation of silica by a polymer catalysed hydrolysis of different silica precursors. The study also concentrates on differentiating polymer template based and template free formation of silica shell and explores formation of capsules based on the properties of the polymer increasing the atomic efficiency thereby incorporating principles of green chemistry and making the whole process economically efficient and environment friendly.

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Trisulfide amphiphiles as actuators to control phytantriol lipid self-assembly

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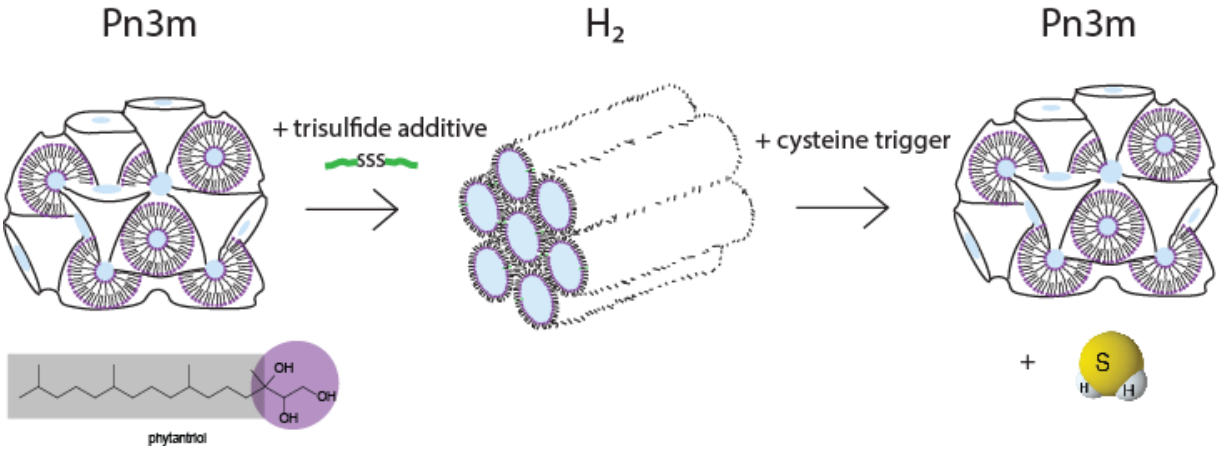
Stimuli-responsive nanomaterials are of increasing interest as researchers look to address drug delivery issues such as those associated with off-target effects. Our research focuses on lipid based nanostructured materials. These materials can be employed as biocompatible, multicompartmental matrices which can accommodate drug molecules with a wide range of physicochemical properties.[1] Manipulating environmental variables, such as temperature and pH, and the incorporation and activation of stimuli responsive molecules and nanoparticles, can enable switching between different liquid crystalline phases which in turn provides the opportunity to trigger and control the release of encapsulated material. In the current study we aimed to create thiol responsive lipid nanostructures by the incorporation of a thiol degradable trisulfide based amphiphile. Using synchrotron small angle X-ray scattering we found that the initial lipid phase formed was dependent on the concentration and structure of the additive. Furthermore, upon the addition of a thiol trigger we observed H_2S release and in some cases an additional lipid phase change. The potential for thiol specific concomitant release of H_2S and encapsulated material makes this approach attractive to formulation scientists looking for controlled drug release.



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