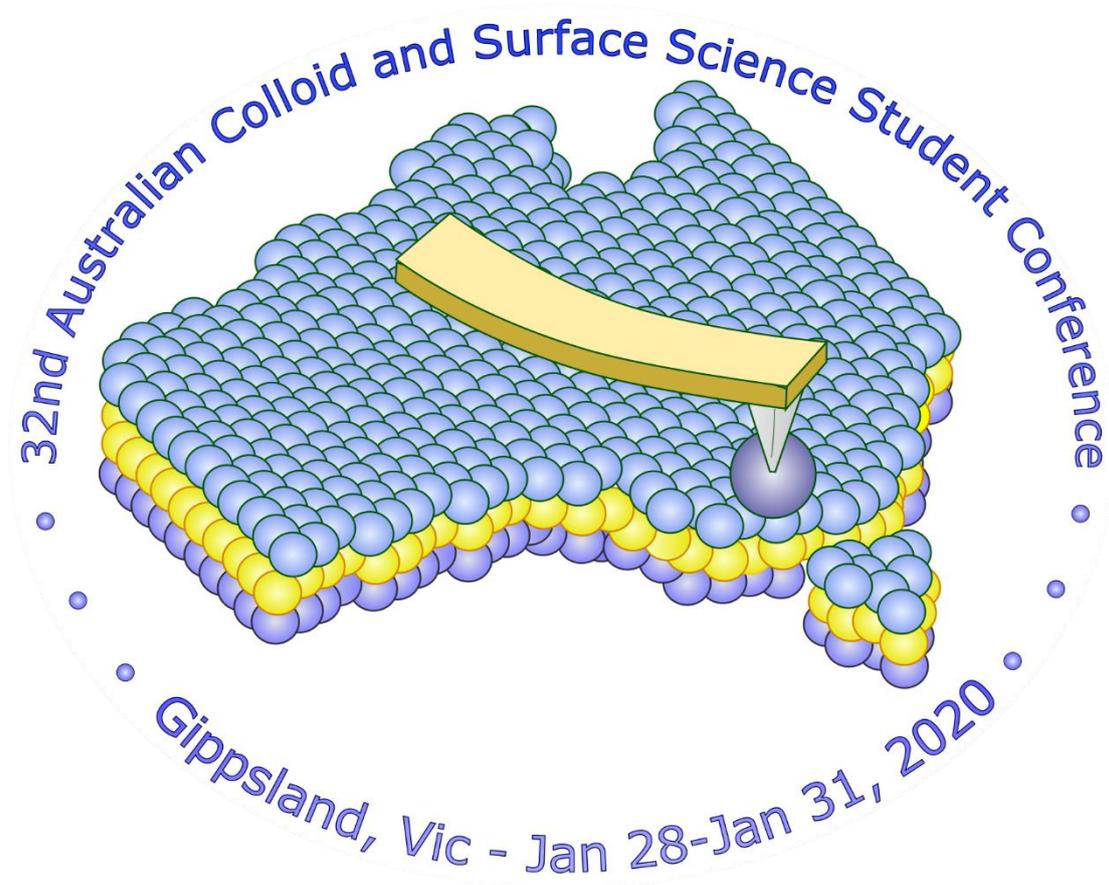


Abstract Booklet

32nd ACSSSC

Jan 28th – 31st, 2020

Federation University, Gippsland, Victoria



32nd ACSSSC - Plenary Speakers List

Dr. Carla Meledandri - The University of Otago, New Zealand

Presentation Title: Nanomaterials for Dental Applications: From Academic Innovation to Commercialisation.



Bio: Carla Meledandri is a Senior Lecturer in the Department of Chemistry at the University of Otago and a Principal Investigator in the MacDiarmid Institute for Advanced Materials and Nanotechnology. She obtained her PhD in Chemistry in 2009 from Dublin City University and held a postdoctoral appointment at the same university before moving to New Zealand in late 2009. Her research is directed toward the use of colloid and surface chemistry techniques to develop new functional nanoscale materials. Carla is a co-founder of Silventum Limited, a spin-out company of the University of Otago focussed on innovative nanocomposite dental materials, and she currently serves as the company's Chief Scientific Officer. She was also the 2017 recipient of the New Zealand Prime Minister's MacDiarmid Emerging Scientist Prize.

Prof. Michael Dickey – North Carolina State University, USA.

Presentation Title: Liquid Metals: A Unique Material for Colloidal and Interfacial Studies.

Bio: Prof. Michael Dickey received a BS in Chemical Engineering from Georgia Institute of Technology (1999) and a PhD in Chemical Engineering from the University of Texas at Austin (2006) under the guidance of Professor Grant Willson. From 2006-2008 he was a post-doctoral fellow in the lab of Professor George Whitesides at Harvard University. In August 2008, he joined the Department of Chemical & Biomolecular Engineering at NC State University where he is currently an Alumni Distinguished Professor. He completed a sabbatical at Microsoft in 2016. He has been awarded many awards including the NSF CAREER Award, Sigma Xi Faculty Award, ASEE Southeastern Section New Faculty Research Award and Outstanding Teacher Award of NCSU. Michael's research interests include patterning and actuating soft materials by studying and harnessing thin films, interfaces, and unconventional fabrication techniques.

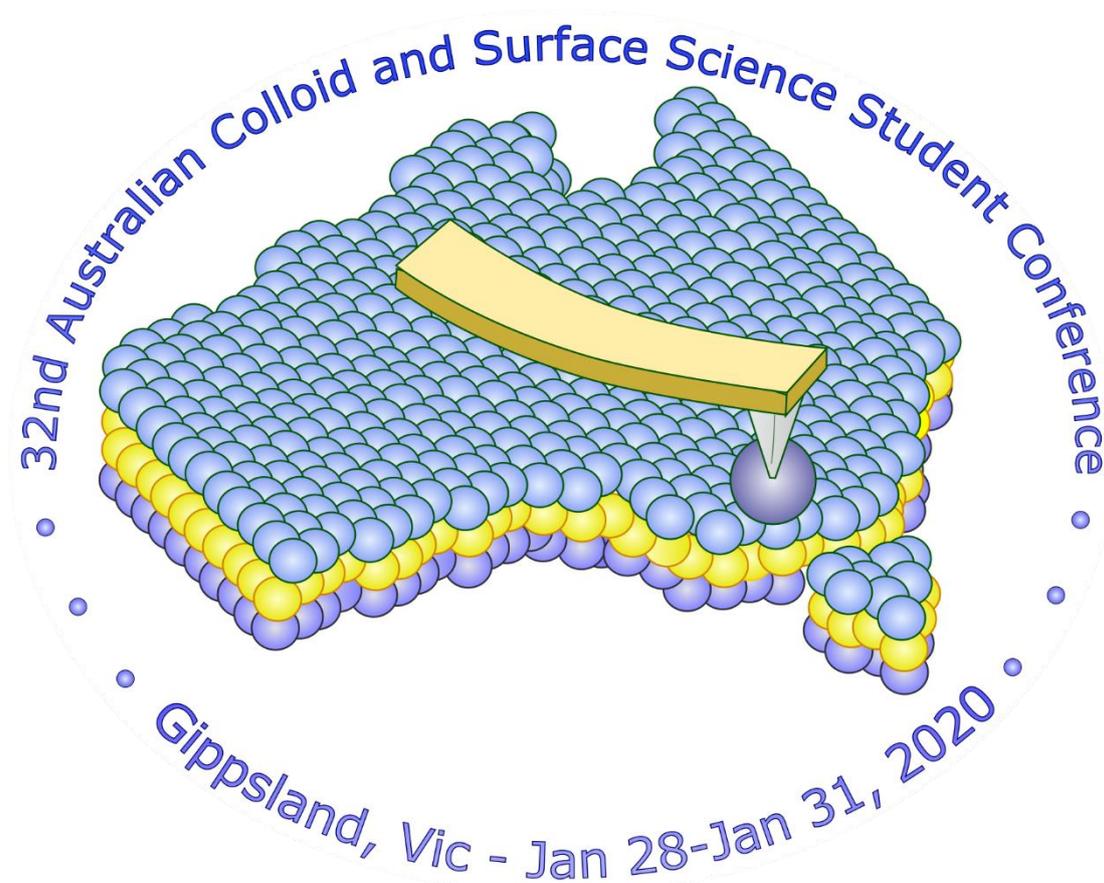


Oral Presentations

32nd ACSSSC

Jan 28th – 31st, 2020

Federation University, Gippsland, Victoria



Synthesis of centimetre-scale ultrathin 2D gallium nitride nanosheets from liquid metal derived gallium oxide

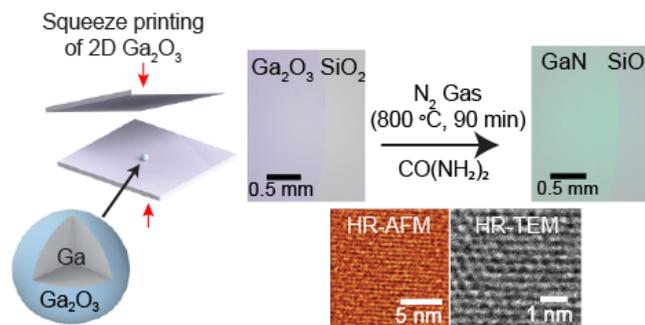
Nitu Syed¹, Torben Daeneke¹, Chris F McConville²

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The wide bandgap material gallium nitride (GaN) in 2D morphology has been predicted to be an interesting target for synthesis due to its enhanced excitonic effects, superior electronic transport properties and quantum confinement effects.¹ Conventional methods based on elemental epitaxial or chemical vapor deposition techniques for synthesizing thin films of GaN are commonly applied.² However, when attempting to synthesize atomically thin samples, these synthesis methods fall short and do not produce 2D GaN films with lateral dimensions exceeding a few hundred nanometers. Therefore, a considerable demand exists for the deposition of ultra-large-area 2D GaN in order to access the capabilities that have been predicted through computational studies. Here, we report an efficient exfoliation technique to deposit ultrathin, centimeter sized 2D GaN using atomically thin gallium oxide (Ga₂O₃) nanosheet derived from liquid metal gallium. Slightly modified van der Waals printing process is adopted to isolate the surface gallium oxide from liquid gallium droplet. The resulting Ga₂O₃ nanosheet will be transformed into 2D GaN using an ammonolysis reaction. The deposited nanosheets were highly crystalline, grew along the (001) direction and featured a thickness of only three unit cells. The as-synthesized wurtzite GaN nanosheets feature an optical bandgap of ~3.5 eV and a carrier mobility of 21.5 cm² V⁻¹ s⁻¹. The method provides a scalable approach for the integration of 2D morphologies of industrially important semiconductors into emerging electronics and optical devices.



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Investigation of the effect of protic ionic liquid solvents on protein and cell stability

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Protein mis-folding is a detrimental effect which leads to inactivation of enzymes, aggregation and formation of insoluble protein fibrils called Amyloids. It is important to understand the mechanism of protein folding, and under which conditions it can be avoided or mitigated. Ionic liquids (ILs) have previously been shown to be capable of increasing or decreasing protein stability depending on the specific IL, IL concentration and which protein. We investigated the secondary structural changes in four proteins lysozyme, trypsin, β -lactoglobulin and α -amylase, in aqueous solutions of 10 protic ionic liquids from 0 to 50 mol% with different cation-anion combination [1]. Some ILs were better for protein solubility and stability than others. The structure-property findings in this study are likely to be applicable to a broader range of proteins and ILs and highlight the large variation in the ability of ILs to support proteins in their native conformation. Following this, we investigated cell viability in ILs, since toxicity is important for many biological applications. Overall the toxicity was highly dependent on the cation and anion combination, with the anion having a stronger affect. It was evident that the PILs can be tailored to vary their toxicities, and this is expected to also be dependent on which cell lines are used.

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Particle size, conductivity, density and electrostatic liquid marbles

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In industry, electrostatics has been employed to remove unwanted particulates from surfaces, for various cleaning and separation requirements.¹ The formation of liquid marbles (LMs), though, is the desired attachment of hydrophobic particles at a liquid interface, increasing stabilisation of the internalised liquid droplet.² It has been shown that the non-contact transport of particles to a liquid interface can be achieved using electrostatics, a dramatically different approach to the liquid-particle contact used in established LM formation techniques.^{3, 4} Whilst advantages of a non-contact process include an increase in viable particle and liquid droplet size ranges,⁵ particle hydrophobicities, as well as marble reproducibility, the interactions between particles and the impact of their various physical properties are not understood when utilising electrostatics.

Here the impact of increasing diameter, conductivity and density of spherical, monodisperse polystyrene (PS) and glass particles, on both the electrostatic extractability and eventual stabilisation of a pendent liquid droplet is investigated. PS particle diameters between 20 and 140 μm highlighted that larger diameters resulted in easier removal from the particle bed due to decreased interparticle cohesive forces, whilst smaller diameter particles afforded increased liquid stabilisation due to increased overall coverage.⁶ Additionally, altering the conductivity of both PS and glass particles was achieved by addition of a thin shell layer of polypyrrole (PPy), synthesised with various dopants. Increasing the conductivity of the particles increases their ease of extraction from the advancing particle bed, but little impact is observed on the liquid stabilisation. Furthermore, increasing particle density (from PS to glass) decreases the ability of particles to be transported to the liquid droplet.

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Stability of self-assembled Janus dimers in a shear flow: a molecular dynamics study

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Janus nanoparticles have attracted much interest recently because of the way that they interact with each other to self-assemble into complex nanostructures. Theoretical studies indicate amphiphilic Janus nanoparticles experience a torque in a fluid flow due to their slip-asymmetric boundary conditions,¹ and this has been verified by our molecular dynamics simulations.² These theoretical considerations suggest that self-assembled Janus nanostructures might be unstable in a fluid flow. We will present our latest results investigating Janus nanoparticle self-assembly considering slip boundary conditions, and determining the threshold flow velocity to collapse self-assembled Janus dimers.

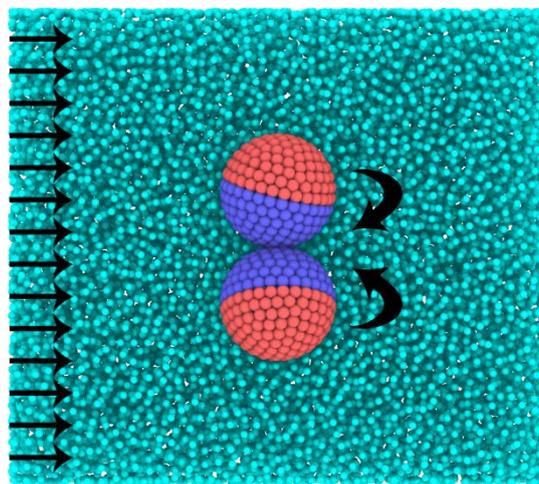


Figure: A self-assembled Janus dimer in a uniform flow experiences torques in opposite directions which may collapse the nanostructure.

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Probing and Pressing Surfaces of Hepatitis C Virus-Like Particles

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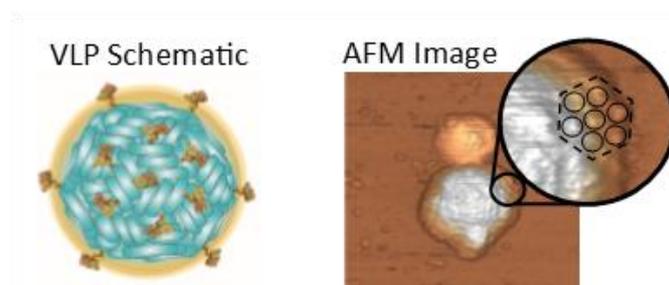
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Enveloped viruses currently present a major risk to human health, and a considerable strain on the global health system. For example, hepatitis C virus (HCV) infects around 71 million people globally, and progresses to chronic infection in around 80% of cases with high mortality rates. There is currently no approved vaccine against HCV. For successful vaccine design, not only the identification of antigenic epitopes, but also the way in which those epitopes are presented to the immune system must be considered. Recent structural determination of viral envelope proteins, alone and in complex with antibodies, has revealed unusual conformations and binding behaviours in the majority of cases. It is therefore important to design and deliver vaccines that present epitopes in native conformation. Recombinant expression of viral structural proteins in cell culture has been successfully used to produce self-assembling virus-like particles (VLPs), which are non-infectious, but present viral proteins in a manner faithful to the conformations found in native viruses, making VLPs ideal vaccine candidates, as demonstrated by approved VLP-based vaccines with efficacy against non-enveloped (human papilloma virus, HPV) and enveloped (hepatitis B virus, HBV) viruses.

Biophysical, biomechanical and biochemical properties are important for virus and VLP interactions with host cells and recognition by the immune system. In this work, we utilize in situ amplitude modulated (AM)-AFM to visualize morphological features of four genotypes of HCV VLPs, currently being developed as a quadrivalent vaccine candidate. Furthermore, the nanomechanical properties of the VLPs were probed using force spectroscopy for each HCV genotype. Ordered packing of the core and potentially envelope glycoproteins was observed on the surfaces of the VLPs. Here, we present the first reported AFM topographical images and biomechanical data for HCV VLPs [1].



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Treatment on Demand: Stimuli-activated Metal Nanomaterials for Antimicrobial Applications

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The development of antimicrobial drug resistance among pathogenic bacteria and fungi is one of the most significant health issues of the 21st century.¹ Recent advances have led to the development of metal and metal oxide nanomaterials, which exhibit antimicrobial properties. Such materials have emerged as promising alternatives to traditional therapies.

In this presentation I will provide a comprehensive summary and critical review of the use of metal nanomaterials as antimicrobial agents. Furthermore, I will present the current state of research surrounding stimuli-activated nanomaterials. Finally, I will present work from our lab surrounding magnetically activated liquid metal nanomaterials as a novel anti-biofilm treatment.

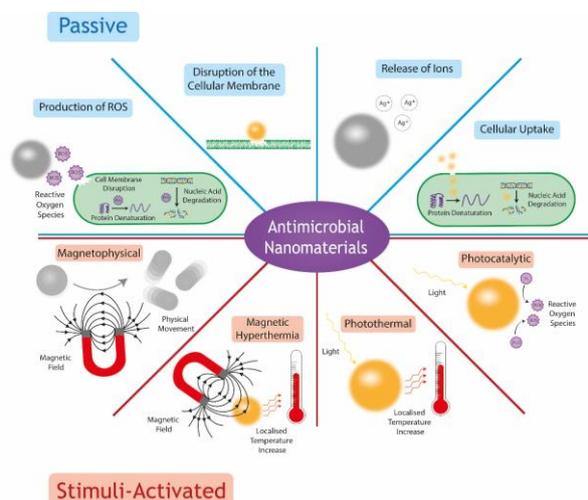


Figure 1. A summary schematic representing the range of passive and stimuli-activated antimicrobial mechanisms of metal nanomaterials.

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Organobismuth complex incorporated nanocellulose hydrogel as potential antibacterial wound gel

Maisha Maliha¹, Rajini Brammananth², Melissa Werrett³, Philip Andrews³, Warren Batchelor¹

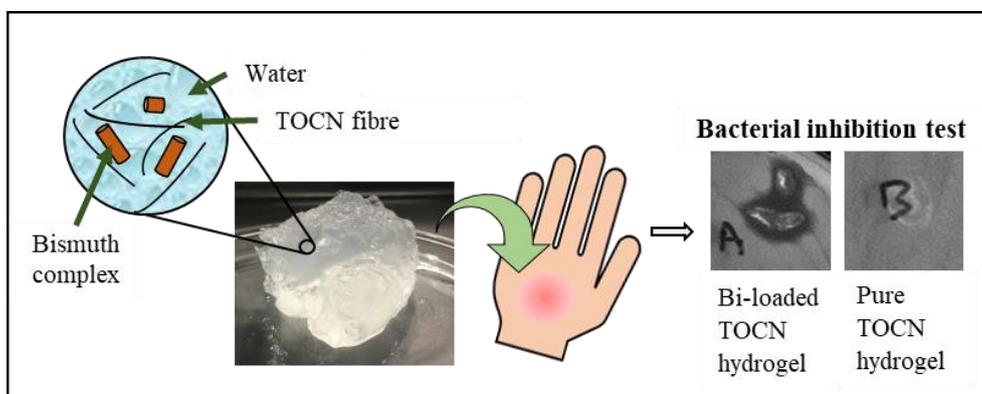
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A large number of factors can complicate the healing of wounds, a major factor being bacterial infection. Due to the high risks of infection, the development of antimicrobial hydrogels for these applications have been gaining interest. These are usually loaded with antimicrobial agents like antibiotics and Ag-based compounds. However, the rapid rise of antimicrobial resistance towards these agents pushes the necessity to look for new and safe alternatives as existing ones are becoming ineffective. The study aims to investigate the use of one such complex as the active agent incorporated into nanocellulose hydrogels. Here, TEMPO oxidized cellulose nanofiber (TOCN) was used to prepare the hydrogel and phenyl *bis*-phosphinato bismuth (III) complex was incorporated into the hydrogel matrix. The hydrogel was characterised using SEM and optical imaging. Antibacterial studies of the composite hydrogel showed complete eradication of bacterial colonies in only 8 hours, 3 hours and 3 hours for MRSA, *Pseudomonas Aeruginosa* and *Acinetobacter Baumannii* respectively. The results also showed the dose dependant effect on the antibacterial performance. Moreover, the rheological properties of the hydrogel have been investigated and shown to be comparable to commonly used over-the-counter burn hydrogels. This study leads towards the designing of a biocompatible, renewable and non-toxic hydrogel, that has broad spectrum antimicrobial activity towards multidrug resistant bacteria.



Lewis Strength Determines Specific-Ion Effects in Aqueous and Non-Aqueous Solvents

Kasimir P. Gregory¹, Erica J. Wanless¹, Grant B. Webber², Alister J. Page¹

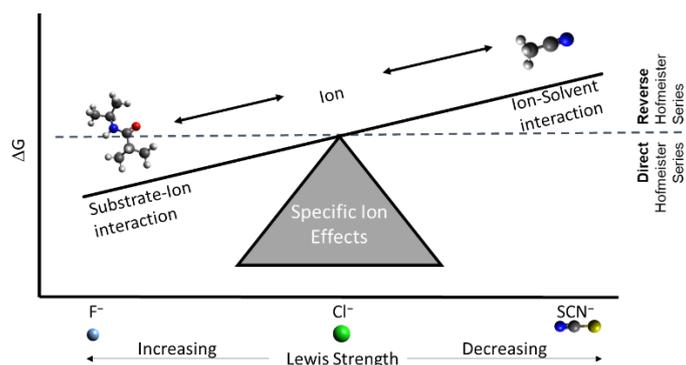
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Specific-ion effects (SIEs) induce or influence physicochemical phenomena in a way that is determined by the identity of the ions present, and not merely by charge or concentration, often categorised according to the well-known Hofmeister series.¹ Examples of SIEs are ubiquitous throughout chemistry and biology, and are traditionally explained in terms of the influence ions have on the structure of water. However, this explanation is unsatisfactory as it is unable to adequately explain and predict frequently-observed series reversals and anomalies. Further, recent experiments have shown that SIEs are observed in non-aqueous solvents.² By modelling solvated ion-N-isopropylacrylamide (NIPAM) complexes, we show that SIEs on ion-NIPAM interaction free energies are observed not only in water, but also in several non-aqueous solvents (methanol, acetonitrile, DMSO). Interestingly, the same trends are observed in the absence of a solvent environment altogether. Counterion effects on ion NIPAM interaction free energies are negligible for dissociated ion pairs, but are evident in associated ion pairs due to the modulation of repulsive ion-NIPAM interactions. We propose a mechanism for explaining reversals in SIEs, based on the competing strengths of the ion-solvent and ion-NIPAM interaction and their relative Lewis strengths.³ This extends existing theories regarding SIE reversals in aqueous solutions, as we show that solvent properties must also be taken into account for SIEs to be predicted in arbitrary solvent environments.



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Solvation properties of protic ionic liquids and molecular solvents

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Ionic liquids (ILs) are highly tailorable solvents with many potential applications. Knowledge about their solvation properties is highly beneficial in the utilization of ILs for specific tasks, though for many ILs this is currently unknown. In this study, we have investigated the solvation properties of 12 protic ionic liquids (PILs) and 9 molecular solvents based on the Kamlet-Abboud-Taft' (KAT) multi-parameter solvation scales. The KAT parameters, which are dipolarity/polarizability (π^*), HBD acidity (α), HBA basicity (β), and the electronic transition energy (ET) were first obtained for the molecular solvents with an extensive set of 11 solvatochromic probe dye molecules. Based on these results the dyes which exhibited the highest sensitivities to polarity changes, and had the greatest chemical stability, were used to determine the KAT parameters of 12 PILs which contained alkyl-, dialkyl-, alkanol-, or dialkanolammonium cations paired with nitrate, formate or acetate anions. Solvation parameters were also obtained for the PILs using the three fluorescent probes Pyrene, Coumarin 153 and Nile Red for comparison. The PILs containing nitrate anions showed the greatest polarity, polarizability and HBD acidity followed by those containing formates and acetates. Almost all the PILs were found to have solvation properties comparable to water and single short chain alcohols like methanol and ethanol. The relative order of the IL polarities was similar for the solvatochromic and fluorescent probes. Through this study, in addition to the well-known distinct solvent properties of alkylammonium cation PILs, the high solvation capability of these PILs has been explicitly shown, which makes this class of ILs desirable for solvent-sensitive applications which require high polarity and H bonding ability.

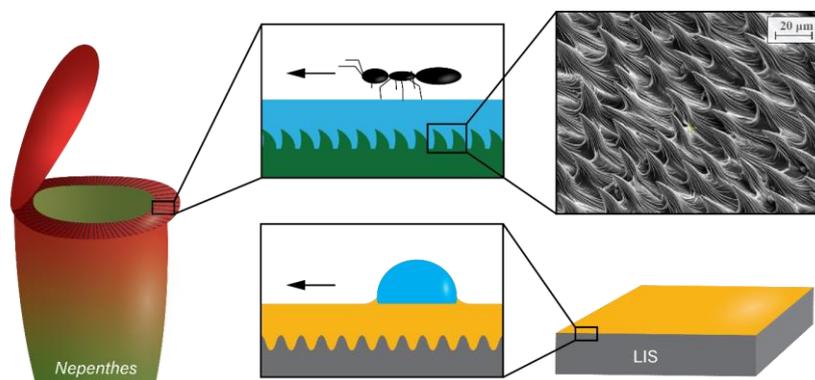
A changing tide: Understanding how an air-water interface depletes lubricant-infused surfaces

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Lubricant infused surfaces (LIS) have emerged in recent years as particularly interesting class of functional materials owing to their potential to stop biofouling in a number of applications such as on the bottom of ships and in biomedical devices.¹ In all applications however, these surfaces are likely to come in contact with air-water interfaces that will contribute to the depletion of lubricant from the surface. Although it is known that the air-water interface contributes to the depletion of lubricant,^{2,3} a detailed understanding has not yet been established. Successful application of these surfaces requires an understanding of their limitations and this work aims to characterise their limitation in the presence of an air-water interface. Utilising a previously developed technique to quantify the local thickness of lubricant on these surfaces using atomic force microscopy force-distance curves,⁴ the depletion of lubricant and subsequent loss of slippery properties is tracked using repeated immersion through a fresh air-water interface. This technique also allows for the *in-situ* tracking of contact angle hysteresis across the surface using a modified optical Wilhelmy plate tensiometer.⁵



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Cool Way to be Cool: Passive Cooling by Porous Polymer

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Passive daytime radiative cooling (PDRC) has attracted worldwide interest since reported as a novel cooling technology that requires minimal energy input.¹⁻² PDRC materials or composite designs demonstrate two key properties: high reflectivity in the solar spectrum (0.3 – 2.5 μm) and high emissivity in other wavelengths, especially at the atmospheric window (8 – 13 μm) where our atmosphere is highly transmissive.³ With these optical properties a PDRC surface is able to minimise energy gain from incident solar radiation and maximise radiative heat loss to surroundings and the universe (2.7 K), hence achieves a net cooling effect.²

Among various established designs of PDRC, diffusive light scattering based on refractive indices difference is a popular way to achieve desired solar reflectivity.⁴⁻⁶ Herein, we prepared a hierarchically porous polymer film from poly(vinylidene fluoride-co-hexafluoropropylene) through a controlled evaporation phase inversion technique.⁷ The film morphology is greatly dependent on variables during formation including environmental condition, polymer-solvent interaction, applicational thickness, etc. We aim to explore the formed hierarchically porous structure by various characterisation methods (including SEM, SANS, USANS, Optical spectroscopy, etc.) in order to gain insight on how to optimise its performance as a PDRC design. Moreover, the polymeric nature of the design enables the potential on further modification which imparts extra functionality than cooling, for example, water condensation.

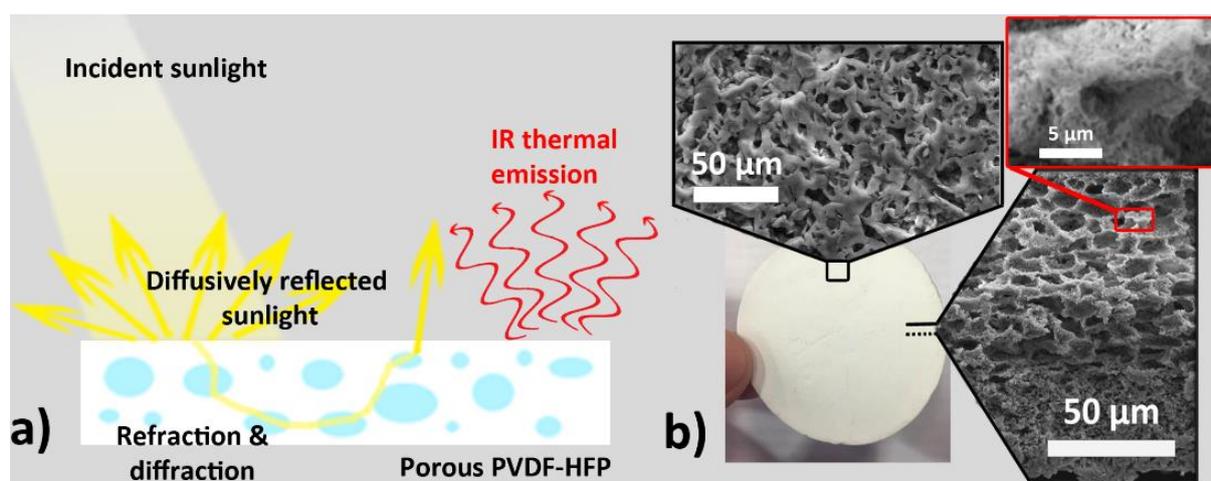


Figure 1. a) Schematic representation of the passive cooling fundamentals. b) SEM images showing the hierarchically porous structure on surface and cross section.

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Functional amyloids as templates for bio-inorganic nanomaterials

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Amyloid fibrils offer a wide range of applications in nanomaterial design, including, drug delivery¹, nano-electronics²⁻³, tissue engineering⁴ and water purification⁵⁻⁶. Nanomaterials designed from functional amyloids retain the advantages of amyloid-based materials, while promoting biocompatibility. However, the use of functional amyloids as building blocks for the development of bionanomaterials has not been widely investigated to date. In this context, we explored the potential use of functional amyloids formed by native neuropeptides, somatostatin and substance P, for the fabrication of bio-inorganic materials. We were able to develop a green synthetic protocol, which is effective, environmentally friendly, safe and simple, to produce gold particles and crystals using functional amyloid nanofibrils and gold salts. As a function of peptide concentration, distinct gold particle morphologies can be obtained. Indeed, different peptide sequences yield different gold assemblies such as gold amyloid gels and gold nanoparticle dispersions. On the other hand, silver-amyloid hybrid nanowires were synthesized, which have the potential to be developed into antibacterial materials. Our findings provide insights into amyloid inorganic hybrid materials, which can be further developed into useful biomedical applications.

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High speed Atomic Force Microscopy for visualizing plasma protein adsorption on silica nanoparticle-based coatings

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The development of materials for medical devices, including implants and other medical consumables, remains a challenging research area due to the immediate adsorption of proteins onto biomaterial surfaces. Because of the higher surface activity of proteins, this initial protein adsorption occurs rapidly and may prevent other favourable biological interactions.¹ This is particularly an issue for surfaces that come into contact with blood, often resulting in blood coagulation, thrombosis and inflammation.² Therefore, a fundamental understanding of initial protein adsorption process on surfaces is of significant interest to effectively design biomaterials for advanced biomedical devices. In this work, we present the use of High-Speed Atomic Force Microscopy (HS-AFM) for visualizing dynamic molecular processes of plasma proteins on biomaterial surfaces.

HS-AFM system is capable of acquiring an image within 50-100 milliseconds (10 - 20 frames/second) with 1-2 nanometer lateral image resolution in liquid. Imaging speed and resolution of HS-AFM enables to obtain a sequence of images of real-time dynamic molecular events in nanoscale. Those single molecular observations have provided an insight to address the dynamics of single proteins in terms of initial adsorption processes, including the moment when they first bind and subsequent formation of a protein layer.

In this research, silica nanoparticle-based coating was used as the substrate, since silica nanoparticles are commonly employed by the coating industry due to their low cost material, mechanical robustness and the possibility of functionalizing the particles with different chemistries. Coatings were prepared on gold mylar by spin coating a colloidal silica solution. Then the silica coatings were functionalized with different chemistries using silanes having specific functional groups (i.e. -OH, -CH₃, -NH₂). HS-AFM imaging of the coatings was carried out while flowing a protein solution through the silica coating.

The presentation will show dynamics and interactions of single protein molecules (fibrinogen and bovine serum albumin) on the silica nanoparticle-based coating (Fig. 1.). In general, height, width, perimeter, area, position and roughness changes of protein molecules/surface were measured in terms of dynamic molecular events observed during the initial adsorption process.

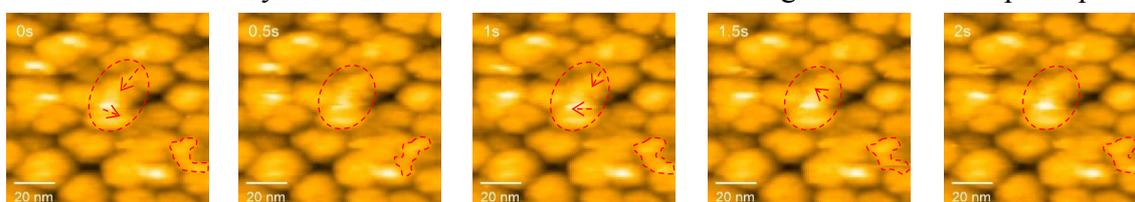


Fig. 1. HS-AFM observations of fibrinogen on silica nanoparticle-based coating.

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Zinc oxide-graphene oxide nanocomposite materials: advancing the antimicrobial properties

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Pathogenic bacteria have emerged as a global health issue in this century. This is largely due to their continued development of resistance towards a range of antibiotic and disinfection methods.¹⁻² Many pathogenic microbes have evolved antimicrobial resistant (AMR) genes, and have been labelled as ‘superbugs’: microorganisms which are resistant to most conventional therapeutic measures. Such pathogens pose serious health threats via the spreading of infectious waterborne diseases, proliferating biofilms and antibacterial aggregations on surfaces of medical appliances, spoliating food impacting water, food and medical sectors.^{1, 3} The aim of this study was to engineer an efficient antimicrobial material based on a zinc oxide nanoparticle (ZnO-NP) doped graphene oxide (GO) nanomaterial with enhanced antimicrobial properties.⁴ These materials provide a nano-scale solution to address the ongoing issues surrounding bacterial contamination. ZnONP-GO (40% w/w of ZnONP/GO) was synthesised using a modified Hummers’ method via oxidising and exfoliating of graphite followed by a series of thermal chemical reactions. The chemical and physical morphologies of the fabricated nanomaterial proved that the unmodified GO has been considerably altered by the inclusion of ZnONPs. The antimicrobial efficiency of the hybridised nanomaterial was evaluated against a range of superbugs including *Escherichia coli* (ATCC 0157:H7), *Salmonella typhimurium* (ATCC 14028) and methicillin resistant *Staphylococcus aureus* (ATCC 700699) following a standard plate count method (SPC).⁵ The proportion of live/dead bacterial cells was analysed using confocal laser scanning microscopy where the interaction of bacteria with the material was observed using scanning electron microscopy.¹⁻² The results recorded that ZnONP-GO nanomaterial could significantly inhibit the growth of analysed strains of AMR bacteria concluding as an efficient antibacterial nanomaterial.

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Overcoming boundary issues: spontaneously enriching 2D nanomaterials at interfaces using hydrotropes

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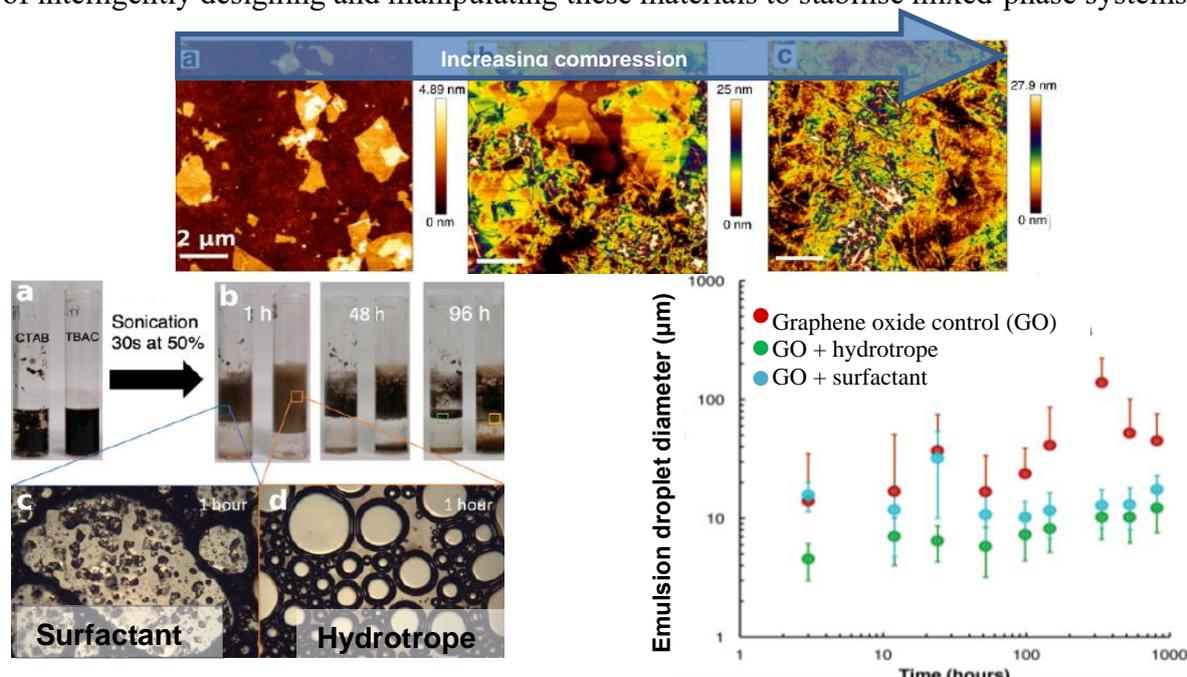
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When two dimensional (2D) materials adsorb to an interface, they can jam that interface through Pickering stabilisation, preventing coalescence and rendering colloidal systems such as emulsions and foams exceptionally stable. Surfactants are often used in conjunction with 2D materials, adsorbing to them in order to facilitate this spontaneous adsorption to interfaces. Surfactants can be environmentally harmful and difficult to remove after use, in addition to being incompatible with some industrial formulations. 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 perform as well as if not better than surfactants at stabilising foams and emulsions when in the presence of the 2D material graphene oxide.¹ We also undertake fundamental experiments such as surface pressure tensiometry, X-ray reflectivity and atomic force microscopy at different levels of interfacial compression to understand how these materials spontaneously self-assemble at interfaces, with the future goal of intelligently designing and manipulating these materials to stabilise mixed-phase systems.



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Synthesis of Nanocellulose Foam: Exploiting their Potential for High Strength Superabsorbent Material

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Nanocellulose is a renewable and biocompatible nanomaterial with high surface area and low density. Due to its surface properties and wide porous structure, nanocellulose based foam can absorb a large amount of water and act as a superabsorbent. The most commonly used commercially available superabsorbent is sodium polyacrylate, which is not biodegradable. Poor biocompatibility and the potential of environmental hazard posed by this petrochemical-based superabsorbent has led researchers to look for renewable options to make biodegradable, renewable cellulose-based alternatives.

In this study, a nanocellulose based superabsorbent has been developed for use in food packaging and personal hygiene products. Bleached Eucalyptus Kraft (BEK) pulp was oxidised and homogenised at high pressure to produce a nanocellulose hydrogel. This gel was lyophilised to prepare the nanocellulose superabsorbent foam. To increase the mechanical strength, a series of physically and chemically crosslinked model nanocellulose foams were prepared and their mechanical and adsorption properties characterised. The hydrogel rheological properties were compared with the dried foam mechanical strength which is correlated with the dried foam absorption capacity. It has been found that although foams using hexamethylenediamine (HMDA) as a chemical crosslinker and polyethyleneimine (PEI) as a physical crosslinker showed increased gel strength, the corresponding dried foams mechanical strengths were not improved. However, blending TEMPO oxidised cellulose with cellulose nano-crystals (CNC) improved the dried foam mechanical strength compared to pure nanocellulose foam. A reduction in comparative absorption capacity was observed. However, mechanical strength is critical to wet durability, thus some absorption capacity can be conceded. This presentation will analyse these novel cellulose based superabsorbents and how their absorption capacity and mechanical strength can be tailored by controlling addition of crosslinker and CNC to govern their structure-property relationships.

Study of Particle Deposition Dynamics in Microfluidic Channel by Resonance Imaging Microscopy

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Transportation of colloidal particles is essential for many industrial applications, such as waste water treatment, coatings, catalysis, emulsions in food industry, etc. In the course of the transportation process, one of the key aspects is particle deposition onto the surfaces, which can be beneficial based on the applications, or it can have adverse effects on the process. Therefore, it is crucial to understand why and how particles deposit on a surface. However, current literature lacks to provide a comprehensive explanation of the deposition process. Moreover, the deposition behaviour for anisotropic particles can be significantly different compared to the spherical particles.

The current work aims to understand the deposition behaviour of both the spherical and anisotropic micron-sized colloidal particles. A new technique has been developed by coupling Resonance Imaging Microscopy (RIM) with microfluidics to understand deposition dynamics of particles irrespective of shape and chemical properties. The particles are observed at real time using RIM to study their spatial and temporal deposition behaviour in the micro-channel. The results indicating the presence of colloidal forces and advection provide an insight into the adherence of particles with the surface in dynamic flow conditions.

Novel azo-surfactant design and synthesis for the development of a single component photo-rheological fluid

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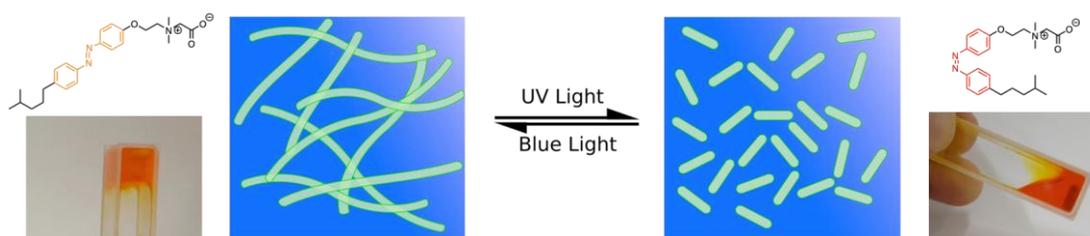
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Photo-rheological fluids are materials that change in their flow properties, such as viscosity and elasticity, when exposed to light of a specific wavelength. In such systems, viscosity changes are generally controlled by the formation or dissolution of wormlike micelles.¹ The unique stimulus-responsive properties of photo-rheological fluids give potential applications in microfluidics, mineral extraction, bioseparations, drag reduction and templated synthesis.²

Most photo-rheological fluids comprise a mixture of surfactants, additives and salts, in order to elicit the desired stimulus-responsive rheological properties. While effective, the complexity of these formulations can cause them to be sensitive to other additives in the system, making their application and incorporation into existing formulations challenging.³

Our work has centred around the development of a novel azobenzene containing surfactant (shown below), capable of forming a photo-rheological fluid without the need for any additives or co-surfactants. Irradiation of this molecule in solution results in a change in the solutions zero-shear viscosity by over three orders of magnitude. This expression of single-component photo-responsive properties represents a first for a surfactant of this type.

In addition to the development of a single component photo-rheological fluid, the fundamental studies from which this compound was derived have given a unique insight into the structure-function relationship of azo-surfactants in solution. This information provides a key tool for future rational surfactant design which, as the effectiveness of this molecule highlights, is a powerful tool for functional formulation development.



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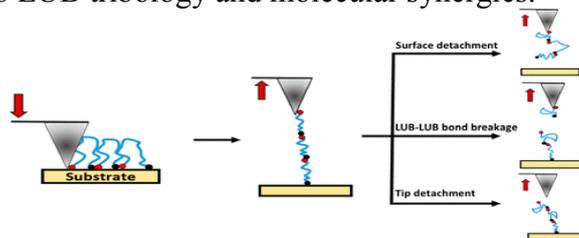
Adhesion and Self-Assembly of Lubricin (PRG4) Brush Layers on Different Substrate Surfaces

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Lubricin (LUB, aka PRG4), a mucin-like glycoprotein, is best known for the significant role it plays in the boundary lubrication, wear protection, and adhesion control systems in human joints. However, LUB exhibits a number of diverse and useful properties, including a remarkable ability to self-assemble into a telechelic brush structure onto virtually any substrate. This self-assembly behaviour has spawned the emergence of numerous non-traditional applications of LUB coatings in numerous areas such as microfluidics, electrochemical sensors, contact lenses, antifouling surfaces, and bionic neural interfaces. Although LUB will readily self-assemble on most substrates, it has become apparent that the substrate has a significant influence on the LUB layer's demonstrated lubrication, anti-adhesion, electrokinetic, and size-selective transport properties; however, investigations into LUB–substrate interactions and how they influence the self-assembled LUB layer structure remain a neglected aspect of LUB research. This study utilizes AFM force spectroscopy to directly assess the adhesion energy of LUB molecules adsorbed to a wide variety of different substrates which include inorganic, polymeric, and metallic materials. An analysis of the steric repulsive forces measured on approach provides a qualitative assessment of the LUB layer's mechanical modulus, related to the chain packing density, across substrates. These modulus measurements, combined with characteristic features and the dwell time dependence of the LUB adhesion forces provide insight into the organization and uniformity of the LUB brush structure. The results of these measurements indicate that LUB interactions with different substrates are highly variable and substrate-specific, resulting in a surprisingly broad spectrum of adhesion energies and layer properties (i.e., chain density, uniformity, etc.) which are not, themselves, correlated or easily predicted by substrate properties. In addition, this study finds exceptionally poor LUB adhesion to both mica and poly(methyl methacrylate) surfaces that remain widely used substrates for constructing model surfaces in fundamental tribology studies which may have significant implications for the findings of a number of foundational studies into LUB tribology and molecular synergies.



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Shaped Particles for Improved Pulmonary Drug Delivery

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Abstract: Particle shape and size can have a strong impact on drug delivery efficiency, affecting cellular processes like phagocytosis and enhancing hydrodynamic deposition. While a number of methods exist to prepare complex-shaped particles in the 10-100 μm size range, smaller particles are needed for efficient pulmonary drug delivery¹. We have previously studied the production of elongated particle shapes by enabling surfactant-induced dewetting to occur simultaneously with droplet crystallization². We optimize the process for micron- and submicron-scale particle production by comparing the dynamics of particle formation with physical models of combined dewetting and crystallization. The models enable us to predict the range of shapes produced, and their lower size limits, as well as linking common process variables to particle production efficiency. We use optical and electron microscopy to study particle morphology and show that the process can be extended to direct production of particles in an evaporating aerosol stream for on-demand particle production and delivery.

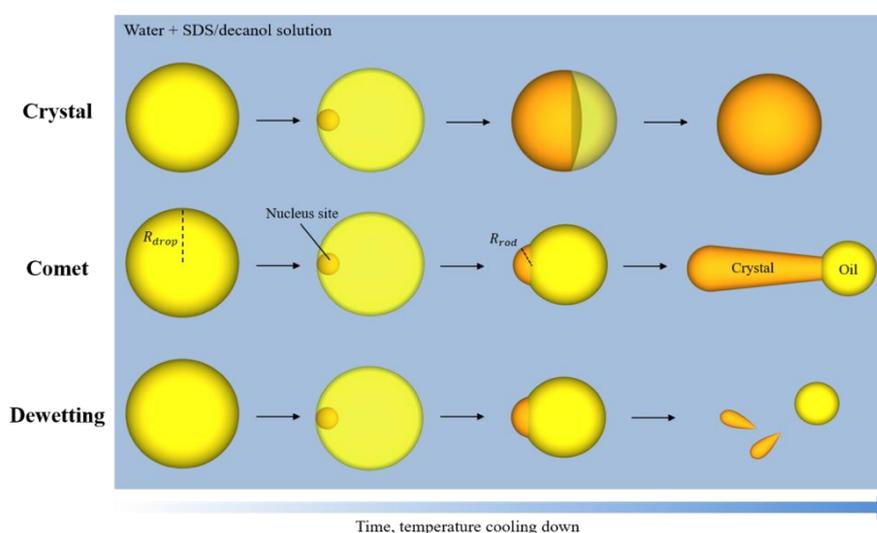


Figure: Three different types of particles made by interfacial crystallization approach.

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Multi-responsive copolymer brushes: interplay of composition, pH and temperature on brush structure

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Grafting of multi-responsive polymers into a brush regime allows for the modification of the interfacial properties of a material through the application of internal and/or external stimuli.¹ Herein an investigation into the responsive behaviour of statistical copolymers of poly(2-(2-methoxyethoxy)ethyl methacrylate) (PMEO₂MA, a thermoresponsive polymer with a lower critical solution temperature (LCST) ~26 °C in water)² and poly(2-(diethylamino)ethyl methacrylate) (PDEA, a pH responsive weak polyelectrolyte with pK_a ~ 7.5)³ is examined. These multi-responsive P(MEO₂MA-*stat*-DEA) brushes were synthesised using surface initiated ARGET ATRP and the temperature and pH response of these coatings tracked with ellipsometry and neutron reflectometry. Numerical self-consistent field theory was used to simulate brush behaviour and compared to the experimental results. Modelling of the reflectometry revealed the presence of a depletion region in the volume fraction profiles. These non-monotonic profiles are attributed to a monomer gradient within the brush profile.

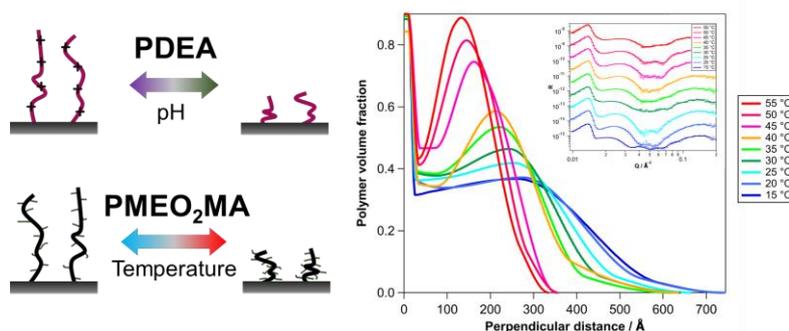


Figure 1. Schematics indicating responsive behaviour of PDEA and PMEO₂MA homopolymers. Right hand figure shows the polymer volume fraction profiles of a P(MEO₂MA-*stat*-DEA) 80:20 mol% brush as a function of temperature at pH 4. Inset shows measured (data points) and modelled (lines) reflectivity data.

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The effect of microstructure on digestibility of micellar casein gels

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The micro- and macro- structure of food materials are an important factor in controlling digestion, which can delay or facilitate nutrient release. Caseins represent nearly 80% of milk proteins and provides the underlying structure of most dairy-based gel products. such as cheese and yoghurt. To understand the effect of gel structure on the digestibility of micellar casein gels, we have investigated the network deformation and degree of proteolysis, as measured by the amount of soluble protein in the gastric fluid over the course of simulated *in vitro* digestion. Casein gels of different structures such as rennet and transglutaminase induced gels with a protein composition of 10% by wt. were formed by a sol-gel transition as a result of a decrease in micellar colloidal stability. An *in vitro* static digestion model was employed with simulated gastric fluids to mimic structural breakdown under acidic conditions (Brodkorb et al. 2019). The protocol was performed with and without gastric enzyme pepsin to elucidate the contribution of the biocatalytic action to structural deformation. Ultra small and small-angle neutron scattering (USANS/SANS) in conjunction with scanning electron microscopy (SEM) enabled structural changes of casein at a micro (micellar) and macro (micellar gel) scale to be followed as a function of digestion time (0, 15, 120 min.). Transglutaminase induced gels exhibited a finer gel network with smaller pores compared to the coarse and porous structure of the rennet induced gels (Fig. 1). Moreover, our scattering results suggest the mode of action for gel deformation with pepsin is a combined effect of particle erosion and network structural rearrangement within the gel particles, whereas without pepsin the protein degradation seems to primarily occur at the surface of the gel particles. With this study, driving mechanisms of digestion in casein gels will be understood in more detail. Our findings will provide a fundamental understanding of the factors causing resistance or susceptibility to the disintegration of protein matrices under simulated gastric conditions.

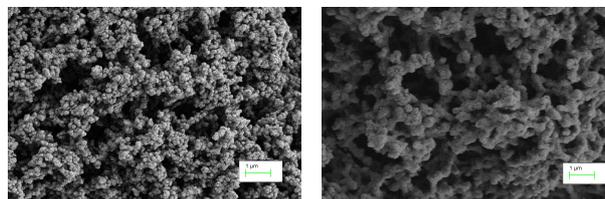


Figure 1 SEM profiles of 10% protein gel and digesta of transglutaminase (left) and rennet (right) induced gels before digestion

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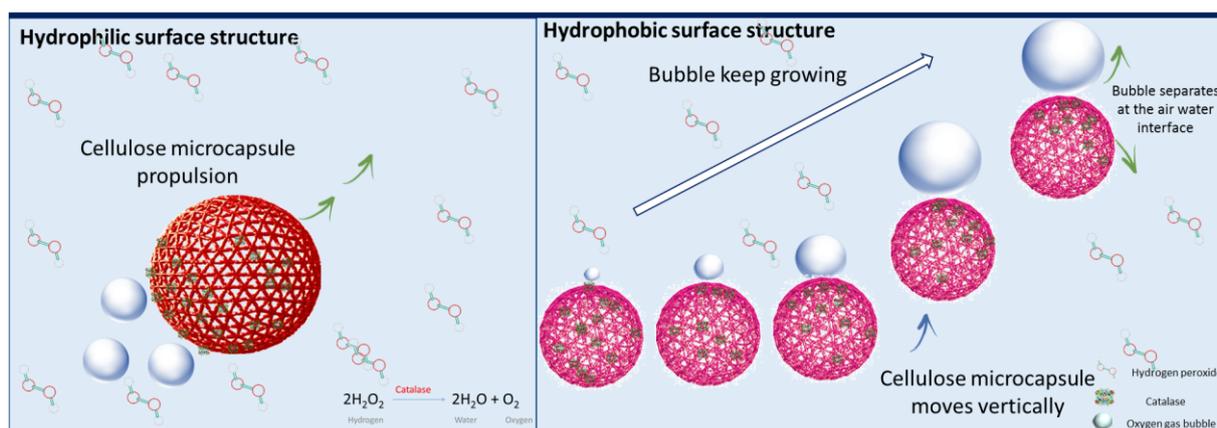
Surface chemistry effects on enzyme-powered nanocellulose micro-swimmers

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Prokaryotic cells can move through liquids or over moist surfaces by swimming, swarming, gliding, twitching or floating (Kumar, Patil et al. 2018). A critical element of such movement is response to external stimuli via complex sensory systems. Biomimicry of the mechanisms of microorganism motility could enable important biomedical and environmental applications including drug delivery, bio-sensing, and removal of toxins. Although multiple modes of propulsion exists in current colloidal swimmers, additional insights can be gained from study of particles with more complex microstructures than the solids often studied. Here we fabricate micro-swimmers from porous capsules of bacterial cellulose, and use MOFs chemistry to attach and protect linked catalase enzyme, that then drives reactive propulsion. Microscopy allows direct observation of the reaction progress and the resulting capsule motion. Particle tracking analysis provides a basis for physical modelling of capsule motion. Oxygen bubbles are generated during catalytic decomposition of hydrogen peroxide, and propulsion by the bubbles occurs via two mechanisms determined by capsule surface chemistry. Bubbles are expelled from hydrophilic microcapsules, driving motion via a reaction force. Hydrophobic microcapsules, however, remain attached to growing bubbles that drive motion as a result of buoyant force.



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Experimental investigation on coalescence of free droplet collisions

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Droplet-droplet collisions play a prominent role in determining the performance efficiency of unit operations, notably solvent extraction, applied in chemical, pharmaceutical, mineral processing and petroleum process industries. Droplet coalescence is governed by aspects such as droplet size distribution, impact velocity, shape deformation and thin film drainage as well as the surface forces between drops, all of which can influence the droplet life times and subsequent mass transfer rates in separation processes. Currently there are studies¹⁻² that have focused on drop coalescence for two drops, where one drop is immobilised on capillary tip and other is in motion. Other studies produce two drops at high velocities to induce collision, however this also induces high velocities in the surrounding fluid, an effect that plays a role in the droplet collision outcome but is difficult to quantify³. Currently, there is no method to repeatably and reproducibly collide two free drops in an otherwise quiescent fluid, with precise control over alignment and impact speed.

In this present work we have developed a novel method capable of performing collisions between freely moving droplet pairs, up to 4 mm in diameter, map the coalescence outcomes as a function of drop size and velocity. Two freely moving droplets, one denser than the surrounding medium and the other lighter, collide after release from capillaries. We map the outcomes of the collisions (e.g. coalescence or bounce) over a wide range of parameters including drop diameter ratio, Weber numbers, collision angle and impact velocities. As part of a wider collaboration, these data are compared to numerical simulations. The goal of this study to enable a clear and systematic approach for the investigation of droplet coalescence by conducting collisions of freely moving droplets at high Weber numbers relevant to industrial scenarios in most liquid-liquid process systems.

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Anion-Controlled Nanostructure and Alkanol Self-Assembly within Biocompatible Ionic Liquids

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Ionic liquids (ILs) are often composed of low atom economy and halogenated organic ions, causing concerns around their sustainability to overshadow their novel characteristics. Recently, choline (Ch) salts have been reported to form ILs, which retain favourable traits of protic ILs with improved biocompatibility and almost null toxicity.^{1,2} We have prepared 6 ChILs (Lys⁻, Phe⁻, Asp⁻, Asp²⁻, lactate, and iso-butyrate), and probed their liquid nanostructure using X-ray and neutron scattering.

Small and wide-angle X-ray scattering from ChILs (Figure 1a) showed the nanostructure depends strongly on anion amphiphilicity, indicated by the low-angle scattering peak at $q = 4\text{--}5\text{nm}^{-1}$. Macroscopically, we observed this is associated to their miscibility with linear alkanols, which led us to the closer examination of intermolecular interactions and molecular arrangements in these ionic-molecular hybrid systems. The outcome (Figure 1b) revealed bicontinuous nanostructures comparable to those seen in alkyl-PILs + alkanols mixtures.^{3,4} Overall, This work uncovers the relationships between miscibility, nanostructure, and anion amphiphilicity in this new generation of biocompatible ILs.

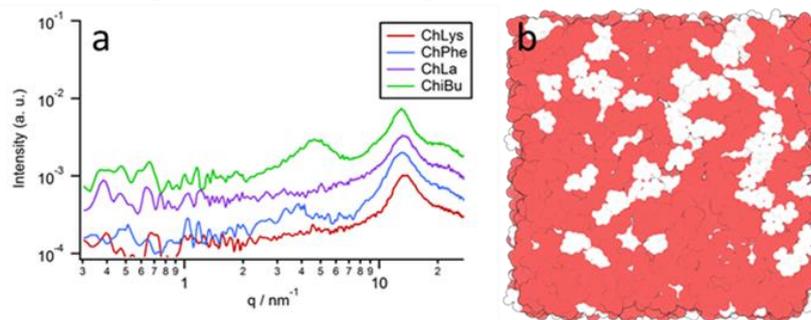


Figure 1. a) SAXS/WAXS patterns of ChLys and ChLac (polar), ChPhe and ChiBu (amphiphilic); b) simulation based on neutron diffraction data showing 1-butanol in ChPhe.

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Single Cell Analysis of Cell-Material Interactions for Discovery of Phenotypic Disease Biomarkers

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Single-cell analysis has emerged as a potential technique for the identification of personalized cancer treatments since heterogeneity in tumors commonly fuels deterioration and resistance to treatment (Dagogo-Jack and Shaw, 2018). Although this heterogeneity comes through genetic and phenotypic variations, phenotypic features provide the advantage of universally applicability and their reflection of the cell's molecular expressions (Sant et al., 2017). However, the relative importance of factors influencing phenotypic heterogeneity and their subsequent impact on genetic variations remain unclear to present them as a universal biomarker.

For instance, the force-induced mechanical changes of the cell and its surrounding microenvironment such as cell stiffness, adhesion dynamics and physical molecular interactions with the extracellular matrix can be delivered as a live-cell phenotypic biomarker as they determine the adhesive and migratory ability of cells in cancer metastasise (Kumar and Weaver, 2009). Hence, a systematic integrative analysis of such live-cell phenotypic biomarkers with the combination of genomic tests would be the key to address intratumor heterogeneity.

The presentation will highlight the importance of cell-extracellular matrix interactions at the single-cell level to develop novel phenotypic cancer biomarkers. Besides, we present the preliminary stage of our project focusing on measuring changes in single-cell properties using AFM in response to the extracellular matrix. We are currently developing a microwell array system as the platform to combine AFM data with other downstream analysis such as gene sequencing.

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The role of relative hydrophobic and hydrophilic chain lengths of diblock copolymer collectors, on the surface tension modification, flocculation and flotation of nuclear waste suspensions

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Flotation has been proposed as a low footprint, high efficiency separation process for rapid dewatering of waste sludges such as $\text{Mg}(\text{OH})_2$, which are similar to those at nuclear fuel management sites, where corrosion processes have degraded fuel cladding. The technology is advantageous as it could effectively be retrofitted into existing waste management facilities at the Sellafield nuclear waste management site. The simplicity (no moving parts) and size of this technology coupled with low cost of construction could be rapidly deployed to aid in risk and hazard reduction decommissioning operations with minimum impact to secondary waste generation. Previously, sodium dodecyl sulphate has been deployed as a collector agent to increase the hydrophobicity of $\text{Mg}(\text{OH})_2$ suspended fines, but extraction was restricted due to hydrodynamic limitations (low extraction of particles $< 20 \mu\text{m}$). These surface-active collectors also increased foaming which reduced the effectiveness of flotation due to excessive water carry over from the bulk particulate suspension. To resolve this problem, various amphiphilic co-block polymers were synthesised via reversible addition-fragmentation chain-transfer (RAFT) polymerisation to produce poly(acrylic acid)-*b*-poly(*n*-butyl acrylate). The hydrophilic poly(acrylic acid) block acts as a flocculation agent to increase the size of the aggregates and the hydrophobic poly(*n*-butyl acrylate) modified the hydrophobicity of the resulting flocs. The high charge density poly(acrylic acid) (PAA) block successfully flocculated $\text{Mg}(\text{OH})_2$ suspensions displaying high fractal dimension suggesting a charge patch flocculation mechanism. The hydrophobic poly(*n*-butyl acrylate) block was varied to different degrees of polymerisation ($D_p = 25-300$) and the effect on flocculation performance was investigated. Performance was measured by several indicators including percentage particulate recovery, volume reduction factor, residual bulk particulate concentration and specific dewatering capacity. Once the effect of hydrophobic block length was established, the hydrophilic PAA group was adjusted to affect the degree of flocculation and thus resultant particle size distribution. The flotation performance of the copolymers were then benchmarked against the traditional surfactant collector agent SDS for comparison to an industry standard.

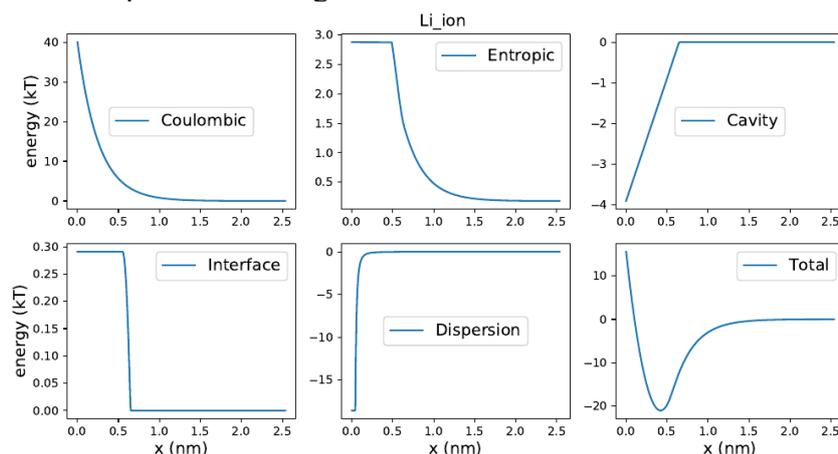
Effect of Ion Cavity and Dispersion Interactions on the performance of Energy Storage Devices

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The performance of energy storage devices mainly depends on two underlying physical phenomena, namely, the ion–electrode interactions, and the dynamics of ions inside those devices. At equilibrium (open circuit), the ion-electrode interaction can be described by Poisson-Boltzmann (PB) equation. PB is based on a continuum solvent model which assumes a point-like ion, immersed in a uniform dielectric solvent medium, in equilibrium with a weakly charged electrode. It does not take into account the finite-size of the ions, their interactions with the neighbouring solvent molecules and most importantly the non-electrostatic interaction between the ions and electrode. As a result, the model is limited to weakly charged electrode and low concentration of electrolyte solution. Another shortcoming of the model is, it can not differentiate between different ions of the same charge. An accurate model which accounts for finite size of the ions and non-electrostatic interaction is crucial to explain the processes taking place in, and predict and optimize the performance of energy storage devices. Here, we present a generalized PB equation based on a modified total free energy of a molecule which accounts for the non-electrostatic interaction terms such as ion cavity, interface and dispersion interactions [1]. We use this model to calculate the energy density and specific differential capacitance of a supercapacitor of 1.2 M concentration with graphite as an electrode, Li⁺ as cation and counter anions of PF₆⁻, BF₄⁻, ClO₄⁻, BrO₄⁻, IO₄⁻ and Cl⁻. We compare our results with that of the classical theory where the quantum dispersion is neglected. This model improves our understanding of the interactions taking place in energy storage devices and helps us in making informed choice of electrode and electrolyte materials.



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Erythrocyte membrane-coated, polydopamine/bovine serum albumin/calcium carbonate particles as a pH-sensitive ultrasound contrast agent

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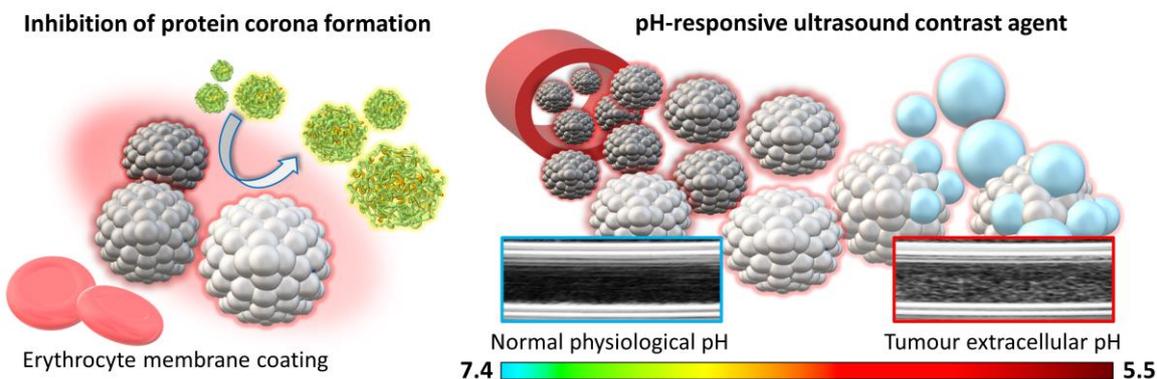
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Biocompatible hybrid polydopamine/bovine serum albumin/calcium carbonate (PDA/BSA/CaCO₃) particles combine the interesting gas-generating and pH-responsive properties of CaCO₃ with the unique optical properties of PDA, which make them suitable for some applications in biomedicine. These materials produce “strong echo-producing” carbon dioxide (CO₂) bubbles upon exposure to low pH environments, which are ideal for contrast-enhanced ultrasound imaging and detection of tumour cells (extracellular pH ~5.5-6.8). However, this particle system suffers from a classical challenge in particle-based imaging agents and drug delivery systems: the formation of protein corona. This protein corona can alter the physicochemical properties, reduce the bioactivity, and change the biological fates of systemically introduced materials.¹

The current work demonstrates the application of erythrocyte-derived membranes as a biomimetic coating for these particles to modulate protein corona formation in simulated physiological conditions. This was accomplished by using two model protein media, foetal bovine serum and human blood plasma. Erythrocyte membrane coating was also shown to increase the ultrasound contrast stability of the generated CO₂. These results indicate that the erythrocyte membrane coating can impart these interesting properties to the hybrid particle system, which may be beneficial in unlocking the system’s full potential in diagnostics and theranostics, and in developing “personalised” drug delivery systems.



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Patterns in dried blood drops

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The coffee ring effect can be observed in many particle suspension systems. This is where the constituents of a pinned sessile drop are deposited preferentially around the circumference of a stain left after the liquid has evaporated. This phenomena has been shown to be highly dependent on the initial particle concentration and contact angle of the suspension. The effect is also seen in the dried deposits of whole blood. As low red cell concentration is a symptom of some types of anaemia, drying blood samples on a range of surfaces and visually comparing the patterns formed is proposed to be a new rapid, low-cost diagnostic tool.

In this presentation we will first present experimentally the effect of the independent variables affecting coffee ring formation with blood. In the second part of the talk, we will model from first principle these patterns.

During blood drop drying, two phases are present: a central fluid region and a deformable porous outer region where the particles (red blood cells) have consolidated. As drying continues this inner region shrinks and the outer region grows. A numerical model was developed to predict the evolution and final height profile in thin droplets containing flexible particles. The model is based on coupling lubrication theory assuming infinite vertical diffusion in the centre region, with a Darcy's law continuum model in the outer region.

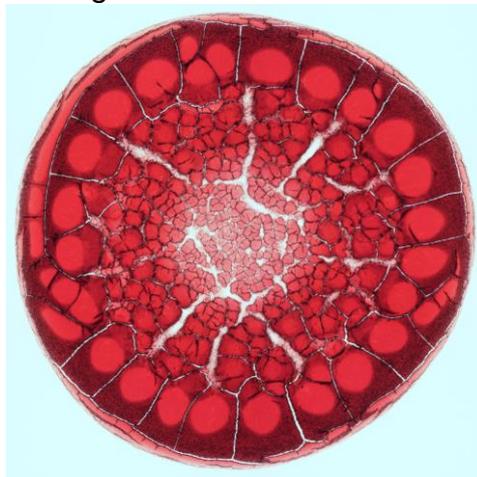


Figure 1: Whole blood dried on glass

Tribology of polymer brush grafted colloidal particles

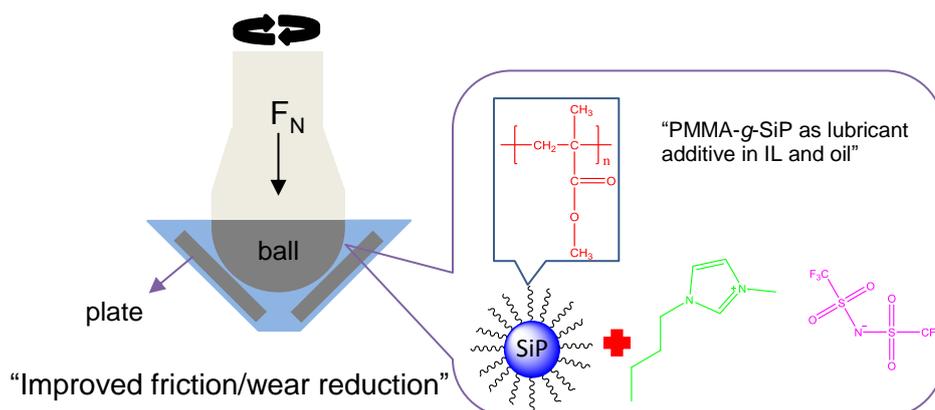
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Ionic liquids (ILs) and nanoparticles are both emerging types of friction modifiers, in which their tribological properties can be further improved by the application of polymer brush.¹⁻³ In this study, the lubricating ability of a colloidal system composed of a hydrophobic polymer brush grafted sub-micron silica particles (with grafting density of 0.56 chains/nm²), known as hairy silica particles (HSPs) as additives in IL and motor oil was investigated. HSPs swollen in IL lowered the sliding friction between steel tribopairs in a ball-on-three-plate tribometer at room temperature, and the lowest friction was observed at the optimum concentration of 0.3 wt% of HSP in IL. Although high temperature tribology of blank motor oil resulted in forcing experiments to be halted, improved friction and wear reduction was reported with the addition of HSP and IL to the oil. The wear analysis from the atomic force microscopy characterized a lower surface roughness and a more uniform wear pattern for HSPs and IL system, and a less sheared surface along with a reduced wear scar diameter for the plate lubricated with HSPs and IL in oil. Exceptional stability of polymer grafted (nano)particles and lubricating feature of polymer brush nominates such colloids as a new class of friction modifiers for practical applications.



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Electrostatic Formation of Liquid Marbles & Aggregates – Conductive Particle Extraction and Transfer

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The electrostatic method of liquid marble and aggregate formation has demonstrated great success due to the ability to transport particles to a pendent droplet over an air gap.¹⁻² The current primary constraint on particle viability for this process is interparticle cohesion, which is exacerbated at small particle size.³⁻⁴ This work overcomes this limitation using copper particles, exploiting their high conductivity to overcome cohesion; we have lowered to size limit to below 10 μm diameter. Furthermore, we detail efforts to quantify the average charge on transferred particles in this process in order to determine a mass coating rate. Greater understanding of this coating process will enable delivery of a controlled mass of particles to a droplet forming a liquid marble or aggregate of precise composition for further use or processing.

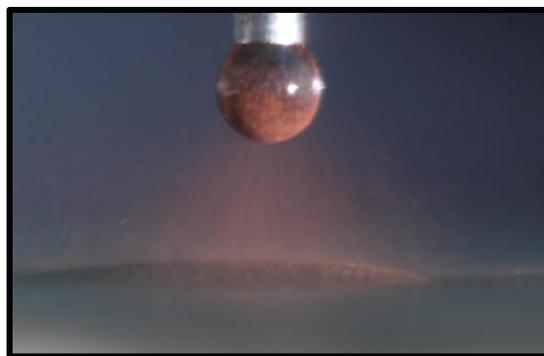


Figure 1. Copper particles being electrostatically delivered to a pendent droplet

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Bulk and Interfacial Diffusion of Nanoparticles in Polyelectrolyte Solutions

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Diffusion of nanoparticles in macromolecular solutions is utilised in a wide range of applications such as enhanced oil recovery, nano-composite materials and targeted drug delivery. The Stoke-Einstein equation used to calculate the particle mobility in a continuous medium assumes no interaction between the particle and the solvent molecules. However, recent studies show that this assumption is no longer valid for nano-particles diffusing in solution containing macro molecules with characteristic length scales comparable to that of the diffusing particle. Particularly in polymer solutions, nano-particles in bulk tend to follow both sub-diffusive and Fickian diffusion dynamics based on the diffusion time scale, thus violating the Stoke Einstein equation¹.

Understanding the diffusion dynamics of nanoparticles in polyelectrolyte solution both at bulk and at interface still remains as a largely unexplored research area. Here, our aim is to investigate the diffusion behaviour of gold nano-particles in sodium polystyrene sulphonate solution both in bulk and at interface as a function of size ratio and polyelectrolyte concentrations. For this study, we use nanoparticle tracking analysis (NTA) to observe the bulk diffusion behaviour of the particle and Total internal reflection microscopy (TIRM) to measure the confinement effects on the diffusion dynamics near a solid-liquid interface. This study will enable us to develop a new diffusion model that links the effects of particle-macromolecule interactions on bulk diffusion to the confinement effects as well as particle-macromolecule interactions on diffusion near surfaces.

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Investigation of a Novel Emulsion Binder for Recovering Ultrafine Hydrophobic Particles

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The recovery and concentration of high value ultrafine particles is challenging, even via froth flotation. Inspired by oil agglomeration, a novel process involving the use of a high internal phase water in oil emulsion binder has been developed to address this issue. The research has focussed on the selective agglomeration of coal, magnetite, and silica.

The use of the emulsion binder leads to a 15-fold reduction in the oil consumption when compared to conventional oil agglomeration. The agglomeration is ultrafast, with the ability to recover hydrophobic particles below 1 μm in size in a few seconds. We believe that the emulsion microstructure is responsible for the efficient and effective particle recovery. The highly concentrated dispersed aqueous phase, which exists as tightly packed droplets, gives rise to a network of thin, permeable oil films. These thin oil films provide a large surface area for hydrophobic particle attachment and hence recovery through the formation of agglomerates. Key parameters investigated include the size of the internal water droplets within the emulsion, which subsequently influence the oil film thickness. Thinning of the films leads to a larger specific surface area of the oil and hence improved recovery of ultrafine hydrophobic particles.

The fast and efficient recovery of ultrafine particles using the emulsion binder can also be attributed to the permeability of these thin organic films towards water. The presence of a salt concentration difference between the internal water droplets and external water leads to permeation of water into the emulsion binder which aids particle attachment. Thus, the water permeation into the emulsion binder was investigated systematically to quantify firstly the flux and its variation with time for different osmotic driving forces, and in terms of the binder geometry and microstructure. The permeation was found to be analogous to the unsteady state diffusional flux across an interface with an inverse square root of time dependence.

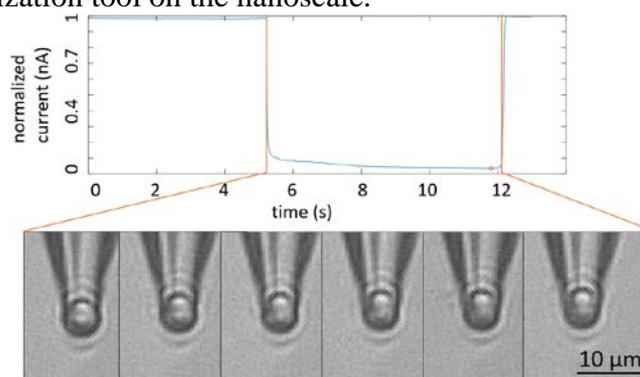
Towards nanomechanical properties determined by pipette ion currents

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Research has shown that biological functions and diseases of various organs and tissues in the human body are associated with their mechanical properties.¹ Meanwhile, interest in extracellular vesicles has re-emerged as they have been found to play a crucial role in intercellular communications and regulatory functions.² Both developments have incited interest in the field of nanoscale biomechanics. A recently-developed technique called microaspiration (MA) which characterizes the mechanical properties of ‘soft’ particles, is adaptable for work in this area. MA functions by applying negative pressure to squeeze samples in and through a micropipette while observing both the particle and the pipette ion current (see figure). Mechanical properties are then derived by applying appropriate models to both datasets. It has been demonstrated that MA can be used to quantify mechanical properties for both biological³ and polymer⁴ samples. A thorough and systematic study is essential to extend the technique down to the nanoscale. As such, polydimethylsiloxane (PDMS) emulsions are excellent test samples due to their tuneable size range which covers both microscale and nanoscale and their well-known material properties. Results from MA experiments can be correlated with data collected from colloidal probe atomic force microscopy (AFM). This comparative study aims to comprehensively adapt MA to become a mechanical characterization tool on the nanoscale.



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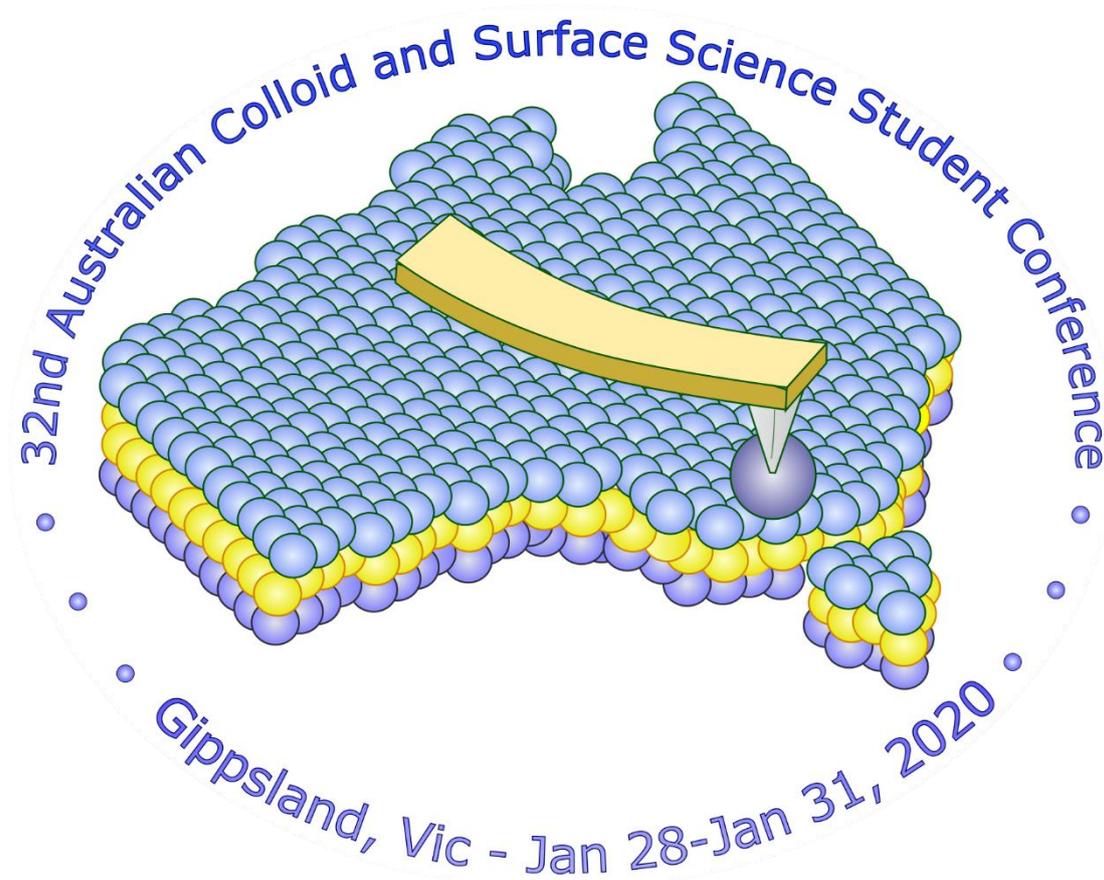
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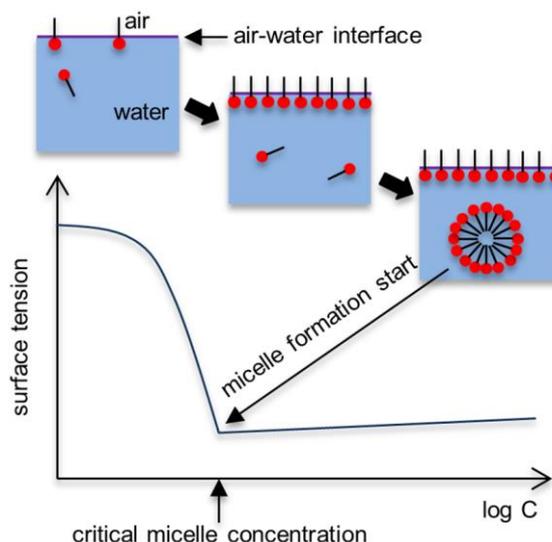
Exploring the effects of ionic liquid mixtures on surfactant self-assembly

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ECR

Ionic liquids (ILs) are regarded as designer solvents because various features such as polarity, cation alkyl chain length, anion nucleophilicity, hydrophobicity, pH, salt kosmotropicity and ionicity can be altered to tailor them for specific applications by changing the structure of the cation and the anion.¹ Simple amphiphiles such as polymers and surfactants can be used as model systems to enhance the understanding of the effects of IL/water mixtures on more complicated structures such as proteins.^{2,3} In this work, surface tensiometry, small angle X-ray scattering, and molecular dynamics simulations have been used to study the self-assembly of amphiphilic surfactants, including monitoring the critical micelle concentration (Figure 1), exploring the size and shape of resulting micelles, and examining the solvent/micelle interactions at an atomistic level. We expect these results to aid in the development of IL mixtures for biomolecule preservation.



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NMR relaxometry: a non-invasive probe of surface phenomena in porous media

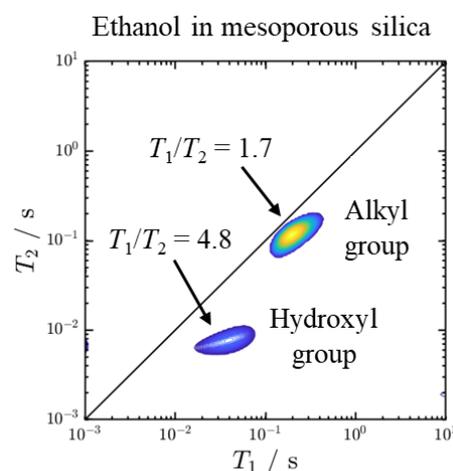
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Understanding the surface interactions of liquids confined to porous solids is of importance across a range of chemical processes including catalysis, separation processes, and the extraction of natural resources. Nuclear spin relaxation measurements offer a non-invasive and chemically selective route for the elucidation of such phenomena. Utilising appropriate NMR pulse sequences and hardware this experimental approach measures the longitudinal and/or transverse relaxation behaviour of the spin system under study, as characterised by the relaxation time constants T_1 and T_2 , respectively. Within the unrestricted bulk phase these time constants conform to a well-defined correspondence with molecular dynamics. For fluids restricted within porous media, however, such measurements are complicated by the pore structure and surface chemistry properties of the confining material, providing a potential route for the characterisation of surface phenomena.

The most widely applied approach for the elucidation of spin relaxation processes in porous media are 2D $T_1 - T_2$ correlation measurements, which provide a detailed description of the relative probability of the system exhibiting a particular combination of T_1 and T_2 times. Such data also provides a robust method with which to quantify the ratio T_1/T_2 , which is now well-established as a measure of the relative strength of surface interactions exhibited by confined fluids. In particular, the use of 2D correlation data allows the clear comparison relaxation phenomena exhibited by liquid mixtures,¹ or by different chemical groups, such as the alkyl and hydroxyl proton behaviours of alcohols (see inset). This talk will provide a general introduction to this rapidly developing field of investigation, and highlight recent advances in the interpretation of NMR relaxation phenomena in terms of adsorption energetics,² and as a potential method for fingerprinting adsorbate interactions at the pore surface.



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Cellulose-Stabilised Emulsions for Pharmaceutical and Home Care Products

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From perfume to milk, from insect repellent to paint, emulsions are an integral part of all aspects of every-day life and yet few people appreciate the underlying chemical interactions.

Often, emulsions are stabilized with non-renewable or harmful chemicals. Like insect repellents that are stabilized by isohexadecane and C18-22 Hydroxyalkyl Hydroxypropyl Guar. Therefore, we investigated a biocompatible and abundant resource for emulsion stabilization; cellulose, which has already been shown to act as a stabilizer for Pickering-type emulsions.¹⁻²

Previous work demonstrated that repellents containing citriodiol could reduce the incidence of malaria in an endemic area.³ We have created a new insecticide formulation composed of just oxidized cellulose nanofibrils (OCNF) and the active ingredient, citriodiol.

Furthermore, we have generated emulsions containing deep eutectic solvents (DES) (e.g. menthol:dodecanoic acid) as the oil phase, also stabilized by OCNF. Little research has been done on DES-containing emulsions and yet they offer huge potential in a range of fields, from drug delivery to microreactors, to templating, especially when stabilized by a biodegradable particle such as OCNF.

Emulsions containing 1.5 wt% OCNF in the aqueous phase and citriodiol or DES (70:30) as the oil phase were made with sonication. Laser diffraction demonstrated long term stability. For example, after storage at 50 °C for two weeks, the average droplet size of the citriodiol emulsion had increased to 2.4 µm. The sample stored at room temperature exhibited an increase to 1.8 µm. The droplet size of the DES emulsion increased from 3 µm to 8 µm after more than four months storage at room temperature. This suggests some Ostwald ripening but not coalescence. Rheological analysis confirmed the emulsions were shear thinning, with a storage modulus higher than the loss modulus.

Altering the concentration of OCNF or including additives changes the stability of the emulsions, as well as the droplet size and rheological properties. This work provides important insights into understanding the role of OCNF in Pickering emulsions, whilst also offering a simple, cheap, and environmentally-friendly alternative to current emulsion stabilizers.

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Stabilization and Crystallization of Lysozyme with Ionic Liquids

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Ionic liquids (ILs) are designer solvents which can help stabilise some proteins. However, it is challenging to understand protein structure in ILs. In this work, we have investigated the structural stability of chicken egg white lysozyme in the protic ILs including ethylammonium nitrate (EAN) and butylammonium nitrate (BAN). FTIR and fluorescence spectroscopy was used to observe the effect of concentration and pH of IL-water mixtures on the secondary and tertiary structures of lysozyme. We observed that lysozyme was precipitated, re-dissolved and stabilized in EAN-water mixtures, and lysozyme had dramatic structural changes in both ILs. Interestingly, the lysozyme was subsequently crystallized in both ILs and the structure was characterized by macromolecular crystallography at the Australian Synchrotron. The crystal structure was modified with IL present, compared to in conventional buffer. The interaction between ILs and lysozyme was discussed. This study provides fundamental understanding on structure-property relationships for future solvent design for proteins.

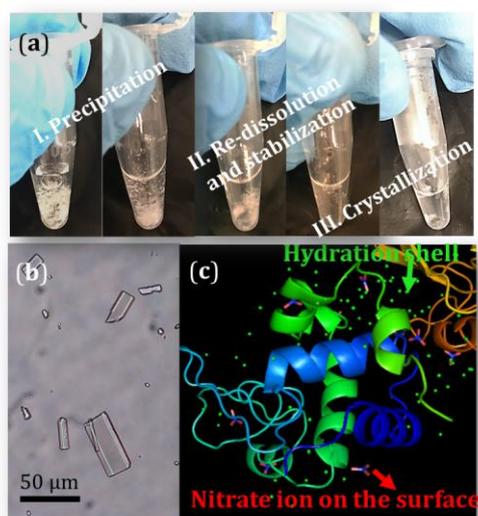


Figure 1. Stabilization and crystallization of lysozyme in nitrate-based ionic liquid-water mixtures. (a) optical image of lysozyme in EAN-water mixtures; (b) microscopy image of lysozyme crystal in EAN-water mixture; (c) lysozyme structure in EAN-water mixture (obtained from X-ray data by MX2 and visualized by PyMOL).

Paclitaxel-loaded self-assembled lipid nanoparticles as targeted drug delivery systems for the treatment of aggressive ovarian cancer

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Nanomedicine has emerged as the next-generation treatment for cancer, offering unique drug delivery properties to eliminate or reduce the generic toxicity of chemotherapeutics via selective targeting and controlled release. Among many classes of nanoparticle-based drug carriers, lyotropic liquid crystalline lipid nanoparticles (LCNPs) stand out due to their ability to encapsulate a wide range of hydrophilic and hydrophobic drugs. These lipid nanoparticles are formed by a self-assembly process, creating internally ordered, nanostructured mesophases such as the inverse bicontinuous cubic phase (cubosomes, CB) in an excess water environment. In the current study, we examined the efficacy of CB as targeted delivery vehicles for PTX in an aggressive ovarian cancer mouse model.¹ These unique CB were made from food grade lipid monoolein (MO) and were stabilised by both Pluronic F127 triblock copolymers and 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-PEGMw=3400-maleimide (DSPE-PEG-mal). A previously established HEY cells-derived ovarian cancer xenograft model was used to study the efficacy of the nanoparticle based PTX treatment.⁴ The MO-based nanoparticles were loaded with 10% PTX and surface-functionalised with Pluronic F127 and epidermal growth factor receptor (EGFR) antibodies. The physicochemical and morphological properties of the nanoparticles were characterized by dynamic light scattering, small angle X-ray scattering, and cryogenic transmission electron microscopy. The efficacy of the drug-loaded nanoparticles were then investigated in vitro using HEY cell viability assay and in vivo using HEY cell-generated ovarian cancer tumour xenograft. This study highlights that the incorporation of a CB-based drug delivery system with metronomic doses of chemotherapeutic agent regimens may be a promising therapeutic approach for the treatment of advanced-stage ovarian cancer patients.

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Dye-TiO₂ interfacial structure in dye-sensitized solar cells using neutron reflectometry

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Solar cells are a widespread, clean and renewable source of energy for humanity's growing power needs. Dye-sensitized solar cells (DSCs) are transparent, flexible, and made from low cost, readily available materials.¹ Compared to traditional silicon-based solar cells, DSCs have higher efficiencies in ambient or dim light. DSCs can be harnessed in areas such as solar windows to generate electricity and offset power costs in buildings.

The dye molecules used in this study are organic, and are structured as donor–linker–acceptor molecules. A range of different donor, linker and acceptor functional groups have been synthesized, including the addition of bulky hydrophobic alkyl chains. At the interface between dye molecules and titanium dioxide (TiO₂) semiconductor, the adsorbed dye molecules harvest energy from light and enters an excited state. The photoelectron is injected into the TiO₂ conduction band, where the electrical circuit begins.

The dye–TiO₂ interface is vital to the efficiency and performance of DSCs, but is poorly understood. This study investigates dye adsorption and packing arrangements at the TiO₂ interface using X-ray reflectometry (XRR), neutron reflectometry (NR) and atomic force microscopy (AFM) instruments at ANSTO, Australia for organic dye structures with different donor and linker groups. Neutron reflectometry (NR) is a powerful technique to examine the dye–TiO₂ interfacial structure in the presence of solvent and electrolyte in order to probe the extent of dye–solvent and dye–electrolyte interactions *in situ*.² While XRR and NR measurements reveal an adsorbed monolayer at the local scale (area ~ 1 cm²), AFM measurements detect small dye aggregates at the surface (area ~ 225 μm²) for all dyes except for the largest and sterically bulky dye studied.

This study demonstrates the importance of dye structure on interfacial properties in DSCs, and may be used to design dyes to optimise properties and solar cell efficiencies, in turn developing DSCs towards full-scale commercialisation.

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Synthesis of 2D TeO₂ from SeTe Liquid Chalcogen Mixture

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Atomically thin crystals that are synthesised in two dimensions (2D) are fundamental constituent for the next generation electronics and optical devices. Reduction in the thickness of the materials enables fitting more components into the circuits and often leading to unprecedented properties arising from the quantum confinement effects. However, for many materials, it is challenging to shrink material dimensions and enhance performances at the same time. Therefore, synthesis and isolation of new high performance materials in 2D, enables realization of this aspiration. As such, we explore liquid chalcogen chemistry for exfoliation of atomically thin layered tellurites (β -TeO₂) crystals for the first time. We demonstrate the exfoliated unit cell of β -TeO₂ from the surface of liquid chalcogen mixtures in low temperatures, featuring bandgap of ~ 3.8 eV. Tellurium oxides and in particular β -TeO₂ are promising candidates for many high performing electronics and optical applications and not previously accessible in 2D. The demonstrated surface oxide exfoliation of the liquid chalcogen mixture presents a promising approach for the development of large area ultrathin chalcogen compounds. Eutectic chalcogen mixture of Se (95 wt%) and Te (5wt%) are prepared. The melting point of the eutectic system is below 200 °C which is less than both Se and Te elements (221 and 449.57 °C, respectively). This allows working with the liquid mixture at lower temperatures than that of tellurium.¹ Similar to metals, an oxide layer forms on the surface of chalcogens. This is evidenced by contact angle change of a droplet of eutectic mixture on a SiO₂ substrate after oxide formation in air (Figure 1a). Based on the thermodynamics consideration, it is predicted that the surface oxides are dominated by element with most negative Gibbs free energy (ΔG_f) of oxide formation which in this case is TeO₂ (Figure 1b). As elucidated in Figure 1c, a droplet was placed and rolled on a SiO₂ substrate. During rolling and dragging of the chalcogen mixture, the naturally occurring oxide that forms on the surface attaches to the substrate via van der Waals forces. Atomic force

microscopy (AFM) of the transferred layer in Figure 1d shows thickness of 1.5 nm layer extending over hundreds of micrometres (Photo in Figure 1c). XPS analysis of the composition is elucidated in Figure 1e. Interestingly, this atomically thin layer is predominantly made of TeO_2 despite abundant of selenium in the eutectic mixture due to more favourable energy of oxide reaction.²⁻³ Presented framework for synthesis of 2D TeO_2 can potentially be extended to other chalcogen compounds setting pathways for the synthesis of novel optoelectronics devices.

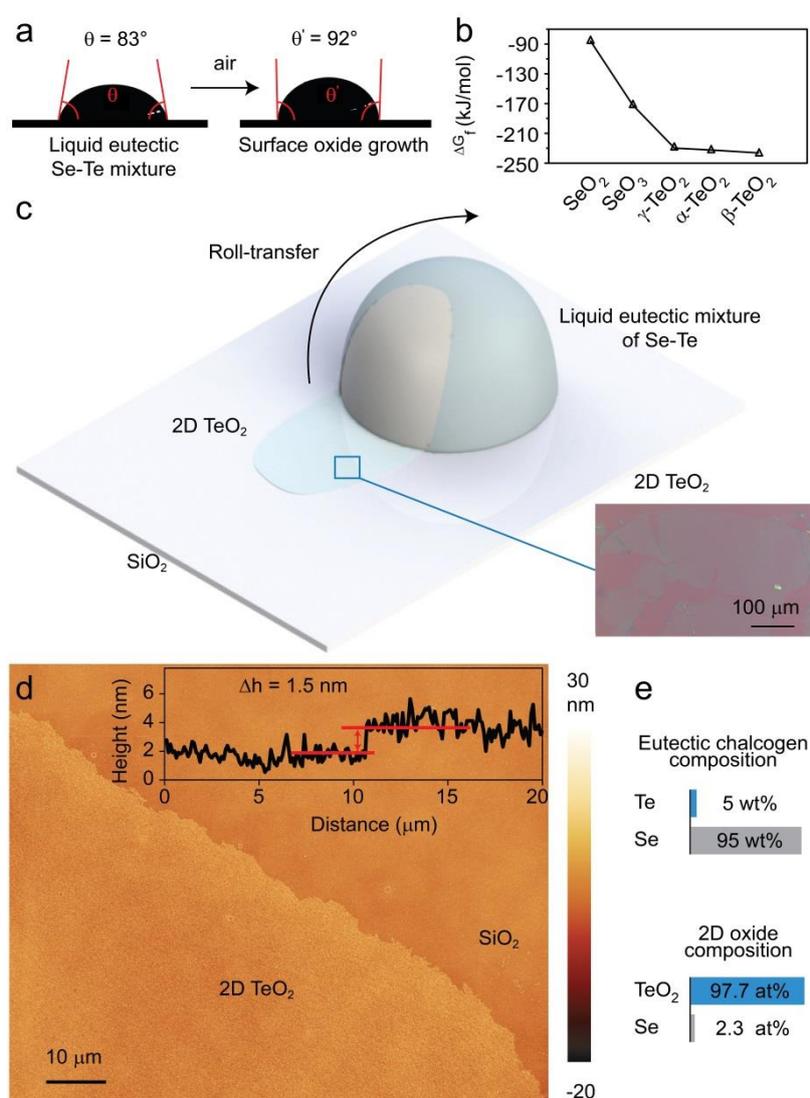


Figure 1. Synthesis schematic and morphology of ultra-thin TeO_2 . **(a)** contact angle of the eutectic liquid mixture of 95 wt% Se and 5 wt% Te chalcogens with SiO_2/Si substrate before and after oxidization in air. **(b)** Theoretical prediction of the surface oxide composition based

on calculated ΔG_f of β -TeO₂ polymorph of tellurium oxide is most favourable to dominate the surface of the chalcogen mixture. (c) Chalcogen eutectic mixture is rolled on a SiO₂ substrate. Its self-limiting oxide layer sticks to the substrate leaving a transferred ultra-thin coating on the surface. Optical image of the printed layer is shown to feature several hundreds of micrometres in lateral dimensions. (d) AFM image of the resulting transferred layer elucidate the 2D nature of the oxide coating. Inset shows height profile with a thickness of 1.5 nm. (e) XPS composition of the transferred 2D layer indicating surface oxide is predominantly TeO₂.

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Mobility of nanocarriers through complex networks

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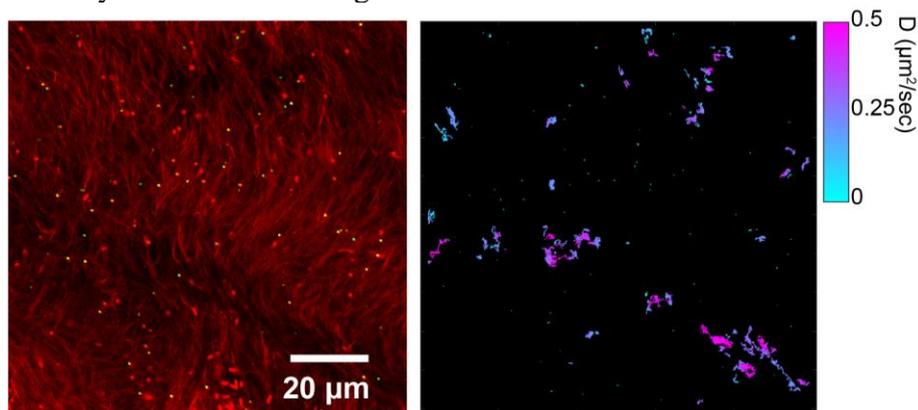
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This work aims to advance our fundamental understanding of how nanocarriers interact with different biological environments, using natural mimic structures as model systems. The underlying dynamics of particle transport through biological networks, like cellular cytoplasm and biofilms, provides significant insights into engineering nanocarriers for optimal targeted drug delivery and cancer treatment.

Confinement by rigid hard obstacles, and compliant soft matrices, alters the transport of nanoscale particles in complex media. Within biological cells, nanoscale cargos diffuse through the crowded cytoplasm and a network of rigid microtubules and/or semi-flexible actin filaments.^{1,2} Similarly, delivering drugs, diagnostics, or therapeutic agents to targeted human tissues requires transport through a rigid extracellular matrix and the extracellular fluid volume,^{3,4} or through the highly selective blood–brain barrier.⁵ In these media, diffusive and transport mobility of nanoparticles is hindered by crowding and by confinement, conditions in which their dynamics are still largely unknown.

In this study, we will utilize optical microscopy techniques, along with image analysis and single particle tracking, to investigate mobility of nanocarriers moving through different complex media, to understand their environmental interactions. Diffusive mobility of nanoparticles, characterized by time dependent mean squared displacement, shows slowed and sub-diffusive dynamics as particles are hindered by the media. The distribution of particle displacements is non-Gaussian, consistent with the spatial heterogeneity of the geometrical confinement imposed by the surrounding media. Such insights enable more accurate prediction of targeted delivery based on knowledge of local tissue microenvironments.



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Nano-Scale Greener Surface-Anchored Anti-Bacterials

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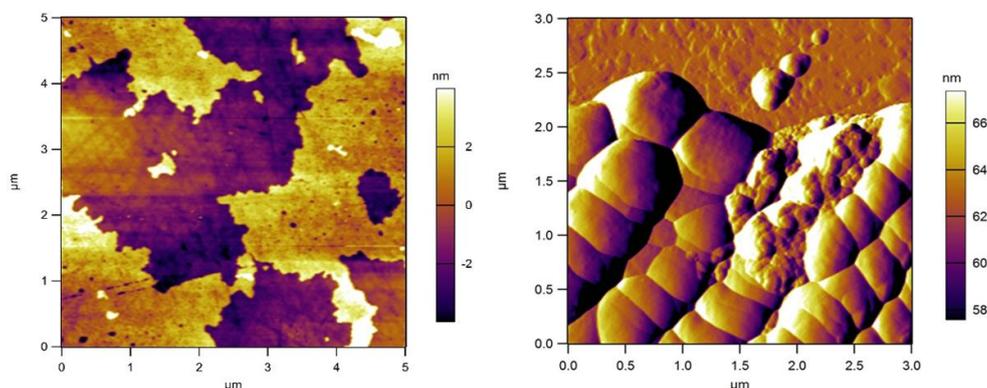
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The global consumer demand for hygienic agents has increased consistently over the past decade and this demand is projected to continue to increase over the coming decade. However, international regulators are reducing the lists of existing approved biocides because of rising sensitivities about human health and environmental impacts. Hence, a gap is appearing between increasing demand and reduced number of approved biocides. Development of entirely new biocides requires expensive and time-consuming regulatory approvals. An alternative greener strategy is to deploy biocides as molecular layers on surfaces, which ensures very efficient access to organisms and which involves extremely low dosages (nano-scale layers) compared to blends and other modes of presentation. Hence, surface anchored biocides have clear greener advantages. This paper reports a series of interfacial studies on surface anchoring silyl-terminated quaternary ammonium salts (AQAS) on various substrates including Quartz (silica), expanded Perlite and thermoset polyurethane thin films. These studies deploy surface and surface region analytical techniques to elucidate monomolecular and multilayered AQAS, including Atomic Force Microscopy (AFM), Angular Dependent X-Ray Photoelectron Spectroscopy (XPS), and Attenuated Total Reflectance (ATR) Infrared Spectroscopy. The molecular layers are observed to form island films of 2- 3 nm thickness on flat substrates (AFM data). Angular dependent XPS spectra in the N1s region (c.400eV and c.402eV) are assigned to oriented first layer of anchored AQAS, and disordered (non-anchored) higher layers respectively. The higher layers are assumed to be a set of three oligomers of AQAS. The C₁₈ alkyl chain in these disordered layers adopts gauche conformations which may shield the quaternary N⁺, contributing to the N1s peak chemical shift in XPS. The quantity of an ideal mono-molecular layer (2-3 nm) of AQAS on a smooth flat substrate is of the order of 10⁻⁷ gcm⁻², which represents an exceptionally low dosage compared to three-dimensional AQAS blends in a polymer substrate. AFM images and microbiological assays confirm the potency of nano-scale systems against *S.aureus* and *E.coli*.



AFM images of covalently bonded surface matt structures of AQAS on quartz (left) and disruption of *S.aureus* colonies by a nano-scale surface layer of anchored AQAS (right)

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This research was conducted within The Biocide Toolbox (BTB) programme which was funded by the NZ Ministry of Business, Innovation & Employment (MBIE)

Size Dependency of Nanoparticles Interacting with Model Membranes

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The rapid development of nanomaterials has led to an increase in the number and variety of engineered nanomaterials (ENMs) in the environment. The expanding production of ENMs has led to serious concerns regarding their impact on human health and environment. Given this degree of exposure, it is striking that implications for environmental and human health remain mostly unknown or poorly understood. Identifying ENMs hazardous to natural organisms is difficult, given the wide variety of nanoparticles (NPs) (e.g. material, size, shape, charge) and the complexity of biological entities (e.g. membrane and media composition)¹. Although there is a vast literature that highlight the biological impact of the NP exposure, a detailed physicochemical description of NP and cell interactions and adverse outcomes relevant to predict in vivo behaviour does not exist. In fact, most of the published studies offer no conclusive nanotoxicological data for in vitro models which might make it possible to predict an in vivo response. In order to be able to distinguish between harmless and harmful ENMs significant progress must be made in understanding the relevant interactions at nano-bio interface.

Since one of the first steps in a toxicological response will be the NP meeting the cell membrane, investigating the physicochemical mechanism underlying the NP-membrane interaction is essential to predict their faith when in contact with membranes. In this work, we quantitatively and qualitatively investigate the strength of the NP-membrane interaction and describe how they can differently interact with the membrane surface by changing a simple material descriptor, the NP size.

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Low temperature lipidic cubic phase as a biomimetic, nanoconfining matrix.

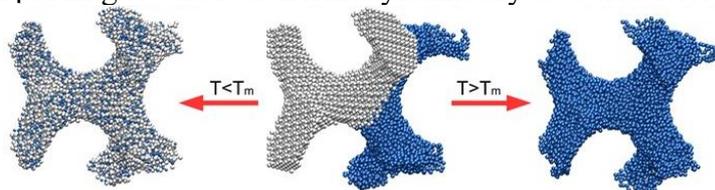
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In aqueous systems, lipids can spontaneously assemble and form supramolecular structures. The topology of these structures is strictly correlated to their molecular shape. Monoacylglycerols are a class of lipids with a unique polymorphism: they are mostly known for their ability to form lipidic cubic phases (LCPs) in excess of water. They are used in areas ranging from membrane biology to drug delivery. A family of synthetic lipids with designed cyclopropyl modifications in the hydrophobic chains was synthesised in order to study the relationship between molecular structure and mesophase behaviour. These lipids show a unique liquid-crystalline phase behaviour, where the cubic structure is maintained at low temperatures, enabling the use of LCP in the crystallisation of proteins in conditions never explored before.¹

Moreover, the small diameter of the water channels of one of the LCPs formed by a synthesised lipid can prevent low-temperature crystallization of water, thus maintaining a state of amorphous water down to 10 K. The study of water and lipid behaviour unveil a complex lipid/water phase diagram, in which bicontinuous cubic and lamellar liquid crystalline phases containing sub-zero liquid or glassy water, or ice emerge as a competition between the two components, each pushing towards its thermodynamically favoured state.²



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Fusion dynamics of cubosome nanocarriers with model cell membranes

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Drug delivery with nanocarriers relies on the interaction of individual nanocarriers with the cell surface. For lipid-based NCs, this interaction uniquely involves a process of membrane fusion between the lipid bilayer that makes up the NC and the cell membrane. Cubosomes have emerged as promising fusogenic NCs,¹ however their individual interactions had not yet been directly observed due to difficulties in achieving adequate resolution or disentangling multiple interactions with common characterization techniques. Moreover, many studies on these interactions have been performed under static conditions which may not mimic the actual transport of NCs. Herein we have observed fusion of lipid cubosome NCs with lipid bilayers under flow. Total internal reflection microscopy has allowed visualisation of the fusion event which was sensitive to the lipid compositions and rationalized by lipid diffusion.² The fusion event in supported lipid bilayers has been compared with those in cells, revealing a distinct similarity in kinetics.

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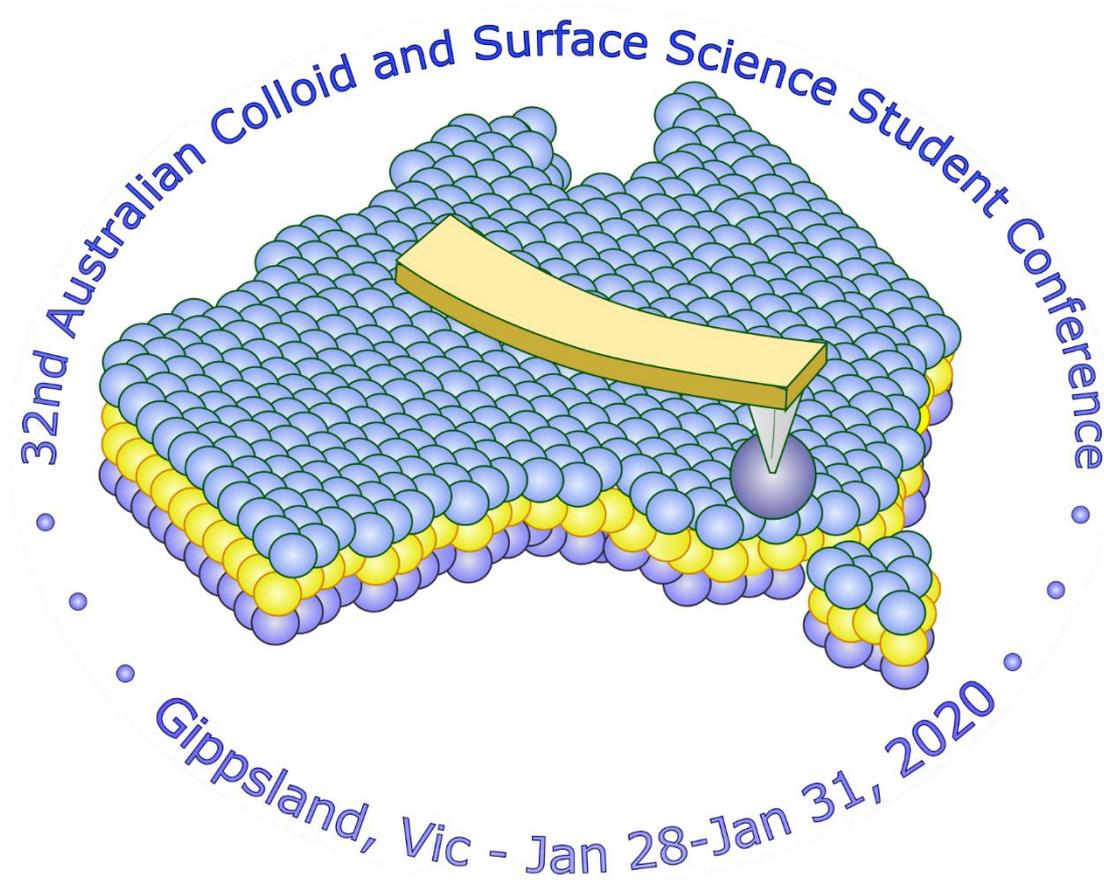
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Poster Presentations

32nd ACSSSC

Jan 28th – 31st, 2020

Federation University, Gippsland, Victoria



A novel method of synthesizing piezoelectric Aluminium Phosphate nanosheets

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Previous research into use of piezoelectric aluminium phosphate (AlPO_4) uses the naturally found bulk material, commonly found in the form of the mineral boehmite. This research uses the method developed by Zavabeti et al.¹ of synthesising 1D and 2D gibbsite and bayerite ($\text{Al}(\text{OH})_3$) as a precursor, and then adapting the method developed by Syed et al.² for the synthesis of gallium phosphate (GaPO_4) via phosphatisation, for the purpose of synthesising AlPO_4 . The AlPO_4 nanoparticles are then tested for piezoelectric properties.

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Development of pH responsive Hexosomes and Cubosomes using novel ionisable lipids

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Lower pH around infected and tumour tissues compared with normal tissues, represents an ideal target for the selective drug delivery. 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 structure, show fast drug release and stronger membrane interaction, in contrast, Hexosomes exhibit much slower release profile (Figure 1). [1]

In this study, we synthesised novel ionisable lipids with an 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 hexagonal or micellar cubic. At lower pH (5.0-6.5), the headgroup is protonated with positive charge, which drives the system to cubic phase for faster delivery of drug and stronger fusion with cancer cell membranes (Figure 2).

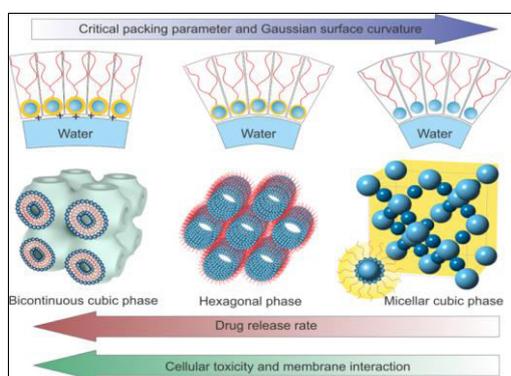


Figure 1: Non lamellar LLC phases and their SAR

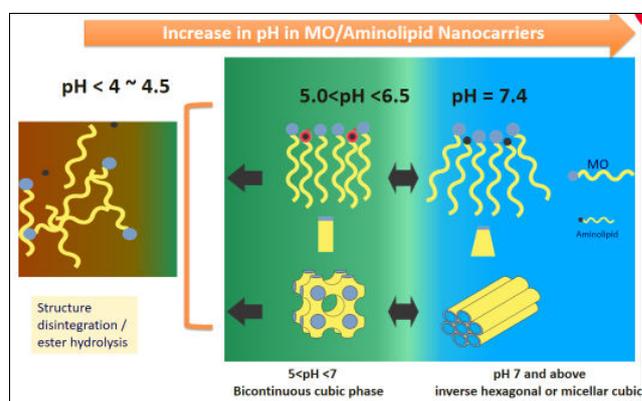


Figure 2: Aminolipid incorporation to MO based nano system

METHODS :

Synthesis and characterisation of Amino lipid esters: Carried out synthesis using oleic acid and amino alcohols, purified using Biotage prep system and analysis by FT-IR, NMR and GCMS.

Nanoparticle formulation and characterization: Various amount of lipid esters were incorporated to MO and pluronic polymer nano system using dry film hydration method.

Particles' hydrodynamic diameter (PS), polydispersity index (PDI), zeta potential (ZP) were measured using dynamic light scattering techniques. Their mesophases were characterized using high throughput synchrotron small angle X-ray scattering (SAXS) at different pH values.

RESULTS AND DISCUSSION:

Total 9 oleic esters were successfully synthesised, purified and analysed.

The lipids were formulated to nanoparticles with various concentration of MO. These nanoparticles appeared stable and their particle sizes were around 200 nm with a PDI range of 0.05-0.2. High throughput SAXS study shows 9 ionisable lipids influencing the mesophase and depending on the head group, we observed pH induced hexagonal to cubic transition at pH < 7.4. The nanosystem investigated herein has the potential therapeutic role for controlled release of drugs in acidic environment.

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Building phase field simulations to investigate properties of cryoprotectants

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The cryopreservation of biological materials is of great importance for those working in areas ranging from the storage of biological materials for scientific research to the storage of blood for medical procedures. In particular the latter has drastic implications for parts of the world effected by natural disasters or caught in war zones where blood supplies can run low or out. Cells are killed when ice crystals form inside or outside them in solution [1], meaning any cryopreservation technique used here must prevent crystallisation and trap the solution in a glass state. A vitrified substance is a liquid that has formed a glass state and can be used to avoid cell damage due to ice formation [2]. The lack of movement keeps potential cell damage to a minimum while remaining in the amorphous phase ensures ice crystals do not grow.

One method for achieving vitrification can be found in nature, where a number of invertebrates are capable of surviving sub zero temperatures using the sugar trehalose [3]. This molecule raises the glass transition temperature of water to above its freezing temperature resulting in glass formation before ice crystals even have a chance to form. However, trehalose does not have a mechanism for crossing the cell membrane. This rules out trehalose as a potential cryoprotectant candidate. Instead a derivative of trehalose that can cross a cell membrane while maintaining its effect on the glass transition temperature would be an ideal cryoprotectant. Simulations can aid in determining which derivative will be a suitable candidate for cryopreservation and in making a comparison to existing cryoprotectants such as dimethyl sulfoxide (DMSO) and glycerol [4]. By equipping researchers with a comparison of different cryoprotectants their efforts can be narrowed to focus on more suitable candidate molecules. This research project aims to improve the methods used to predict the vitrification properties of aqueous solutions at the mesoscopic scale [5].

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Aqueous Protic Ionic Liquids and their ability to stabilise Enhanced Green Fluorescent Protein

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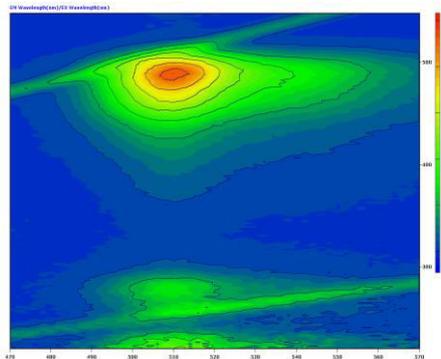
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The use of ionic liquids (ILs) as a media for protein stability has previously been investigated in a broad range of both protic and aprotic ILs, for biotechnological and biomedical applications.¹ It is apparent that ionic liquids (ILs) alter the stability of proteins in solution, either favourable or negatively. Previous studies involving enhanced green fluorescent protein (eGFP) have shown that trace amounts of cholinium based ILs (up to 0.1 mol%), stabilise eGFP, and can potentially be used to purify it more efficiently². However, due to the complexity of most of the currently used systems, it is difficult to determine the exact role the ILs play in the stabilisation of eGFP, and how best to optimise the solvent system.

In this study we are exploring the effect of four ILs, ethylammonium acetate, propylammonium acetate, propylammonium formate, and propylammonium nitrate. IL concentrations between 1 and 50 mol% have been used to assess the effect of ionic strength, and the role of specific ions. Fluorescence spectrometry has been used as a screening method to determine which compositions yield good eGFP stability, based on the intensity of the fluorescent chromophore (see Figure). Size exclusion chromatography small angle x-ray scattering (SEC-SAXS) will be utilised to determine the structure of the protein in solution. These results will be correlated with the chemical and physical characterisations of the solutions. From this study we will gain insight into the role of ILs on protein stability and contribute to the larger goal of being able to design solvents for specific biomolecules and applications.



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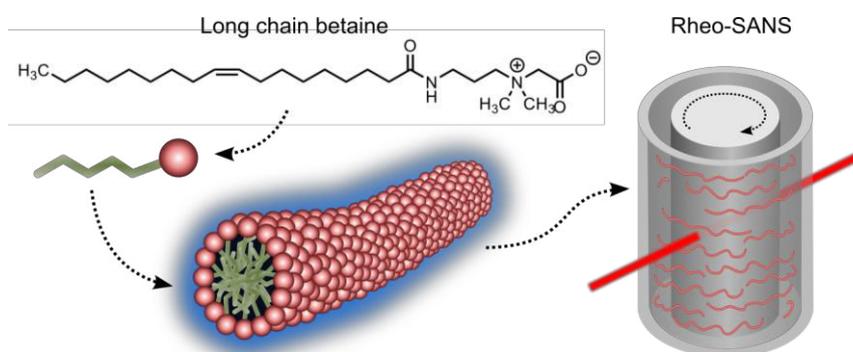
Self-Assembly of Long-Chain Betaine Surfactants: Effect of Tailgroup Structure on Wormlike Micelle Formation

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Amidopropyl betaines are zwitterionic surfactants that exhibit viscoelastic properties, due to their ability to self-assemble into wormlike micelles and other extended micellar geometries. A range of amidopropyl betaine surfactant molecules containing C18 hydrocarbon tails, with differing levels of unsaturation and branching, were synthesised and analysed. The fatty acids used as targets for surfactant tail groups were stearic, oleic, isostearic, linoleic and linolenic acids. Small-angle neutron scattering (SANS), ultra-small angle neutron scattering (USANS) and rheology coupled to small angled neutron scattering (rheo-SANS) were employed to determine self-assembly in solution, micellar geometries and alignment of wormlike micelles under shear. Optimum wormlike micelle formation was achieved for the oleyl tailed surfactant. The more highly unsaturated molecules formed rodlike micelles, whereas the stearic-tailed molecule showed a pronounced Krafft point, and the isostearic-chained surfactant was entirely water-insoluble. These properties indicate that the oleyl-tailed betaine has the most potential to be exploited in applications, particularly where fluid control is imperative. This research has offered new insight into the micellar processes associated with amidopropyl betaines. It is evident that a subtle change in the tail group of amidopropyl betaines can modify the behaviour and solubility of these surfactants.



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Predicting reaction outcome through physical measurements of ionic liquids

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Ionic liquids have been investigated as a potential replacement for molecular solvents due to their unique properties and customisability.¹ Despite this, common application remains inaccessible due to their often unpredictable effects on reaction outcome.²

The reaction between pyridine and benzyl bromide has been investigated in mixtures containing varying amounts of the ionic liquid $[C_4C_1im][NTf_2]$ (Figure 1a, $n=1$);³ there was initially a rapid increase in the rate coefficient, the rate coefficient tends towards a constant value at higher proportions of the salt (Figure 1b). The driving force behind this rate increase, has been attributed to interactions of the lone pair on the nucleophilic nitrogen of pyridine with the cationic charged centre of the ionic liquid.⁴ It would be useful to be able to quantify these interactions and correlate them to reaction outcome, removing the need for such time-intensive kinetics studies.

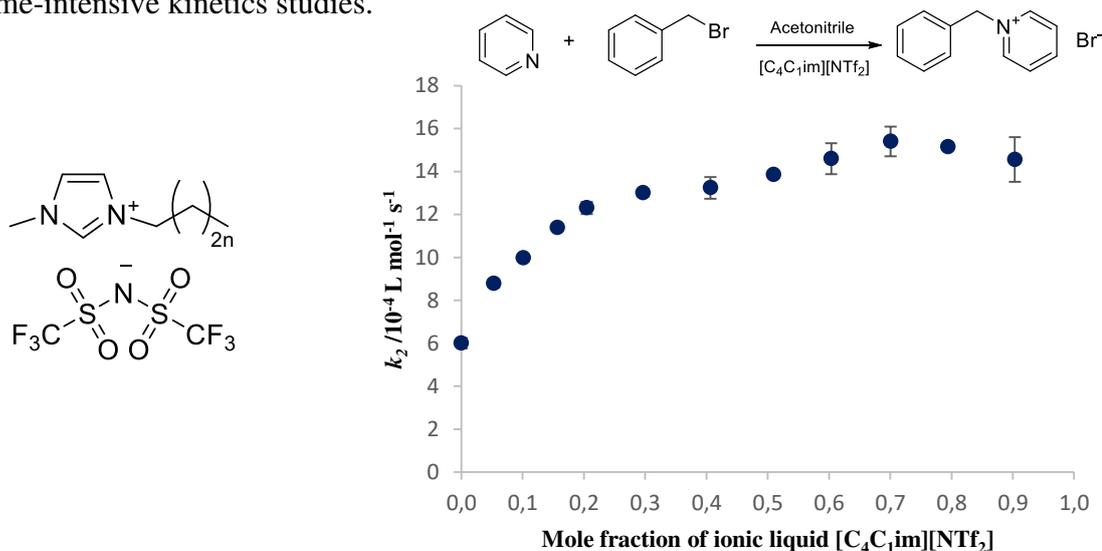


Figure 1: a) $[C_{2n+2}C_1im][NTf_2]$ homologous series of ionic liquids ($n=0-5$)

b) Dependence of the bimolecular rate coefficient of the reaction between pyridine and benzyl bromide on the mole fraction of $[C_4C_1im][NTf_2]$ in acetonitrile, reproduced from Schaffarczyk McHale

This research investigates the effect of varying the length of the substituent alkyl chain on the cation of the $[C_{2n+2}C_1im][NTf_2]$ homologous series of ionic liquids (Figure 1a) on rate coefficient. Through application of NMR relaxometry, a comparatively rapid and financially accessible technique, it is anticipated that changes in solution dynamics may be used in the prediction of reaction outcome without the need to for extensive kinetics analyses.

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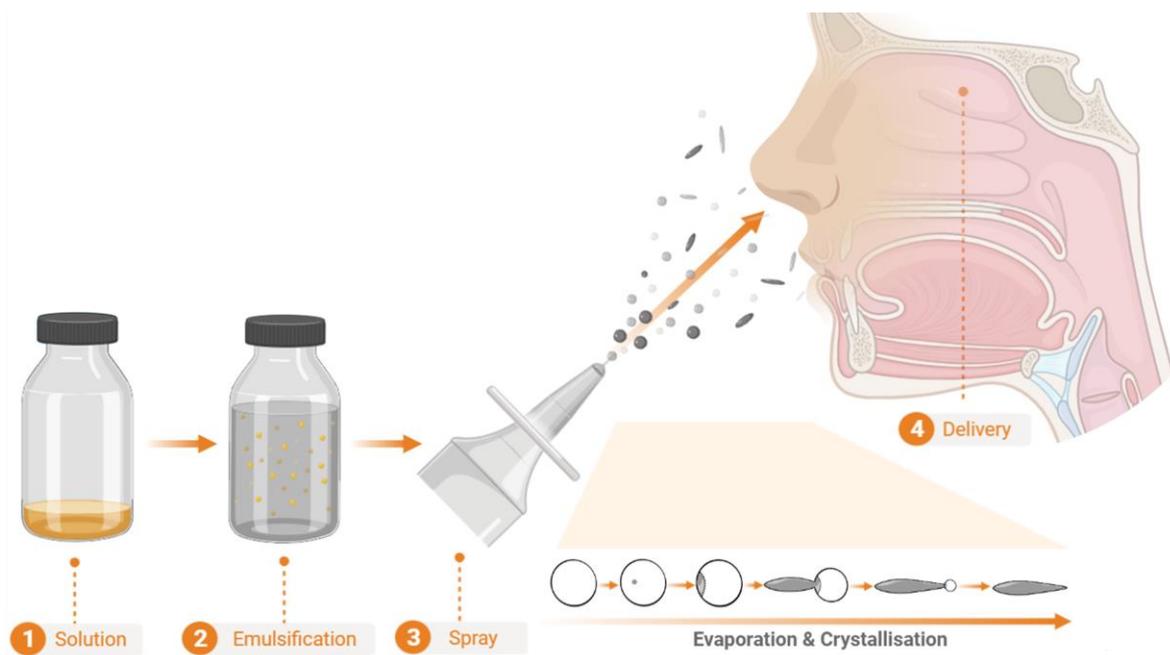
Simultaneous Creation & Delivery of Elongated Therapeutic Particles

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Intranasal inhalable particle delivery is an attractive administration mode for the treatment of both local, systemic and neurological diseases. Particle shape, especially elongated particles are beginning to show great promise in improving therapeutic performance in mucosal environments like the nose, however, there is an unmet need for fabrication methods which do not rely on intensive microfluidics, templating or thermal control. Solvent diffusion from solvent-lipid emulsions offers an ideal, alternative, pathway for creating non-spherical particles by dewetting their own solid crystals from interfacial instabilities during crystallisation. A broad variety of elongated, tapered and novel oscillatory lipid crystal particle morphologies can be produced in this way across broad length scales, ranging from about 3 to 140 μm , with aspect ratios ranging from about 1 to 15. Particle size and morphology can be controlled by surfactant concentration and solvent evaporation rate, and, scale with initial droplet size. By adopting well-established spray-drying and aerosol spray principles, we aim to integrate this method into nasal spray devices for intranasal drug delivery; as an *in-flight* formation process upon spraying, hereby combining both the creation and delivery of shaped therapeutics.



Self-assembly and properties of light-responsive, azobenzene-based liquid crystals

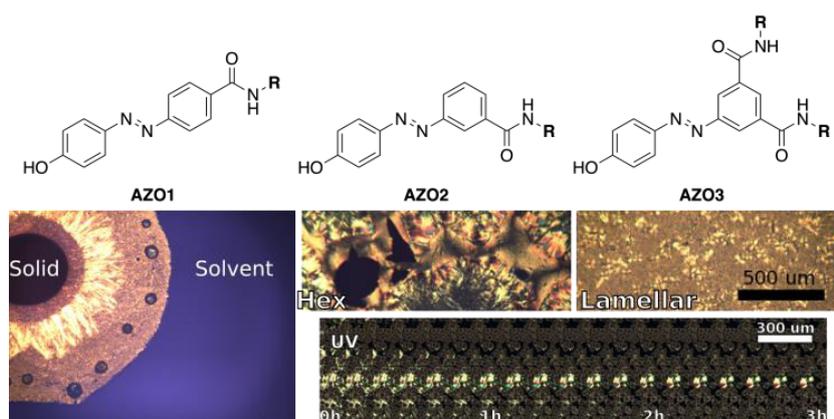
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The azobenzene functional group is known to have a facile and reversible photo-induced *E/Z* isomerization. By incorporating this functional group into molecules, materials can be made that exhibit light-induced changes in their chemical or physical functionality. One particularly interesting class of materials for the investigation of introduced light-responsive behaviour are liquid crystals. Liquid crystals are a class of matter that combines the order of crystalline solids with the flow properties of liquids. The combination of this specific set of properties leads liquid crystals to have applications in a diverse array of fields such as displays, sensors, actuators, protein crystallization and holography.

When introducing azobenzene switches into liquid crystalline systems, it becomes important to understand the molecular interactions that drive the self-assembly and, therefore, function of these multi-component soft-matter systems. Our work explores these interactions using a library of simple azobenzene building-blocks in an attempt to understand these interactions across a range of concentrations and methods of application, from binary (azobenzene + solvent) lyotropic systems to use as minor component dopants in thermotropic liquid crystals and surfactant mesophases.



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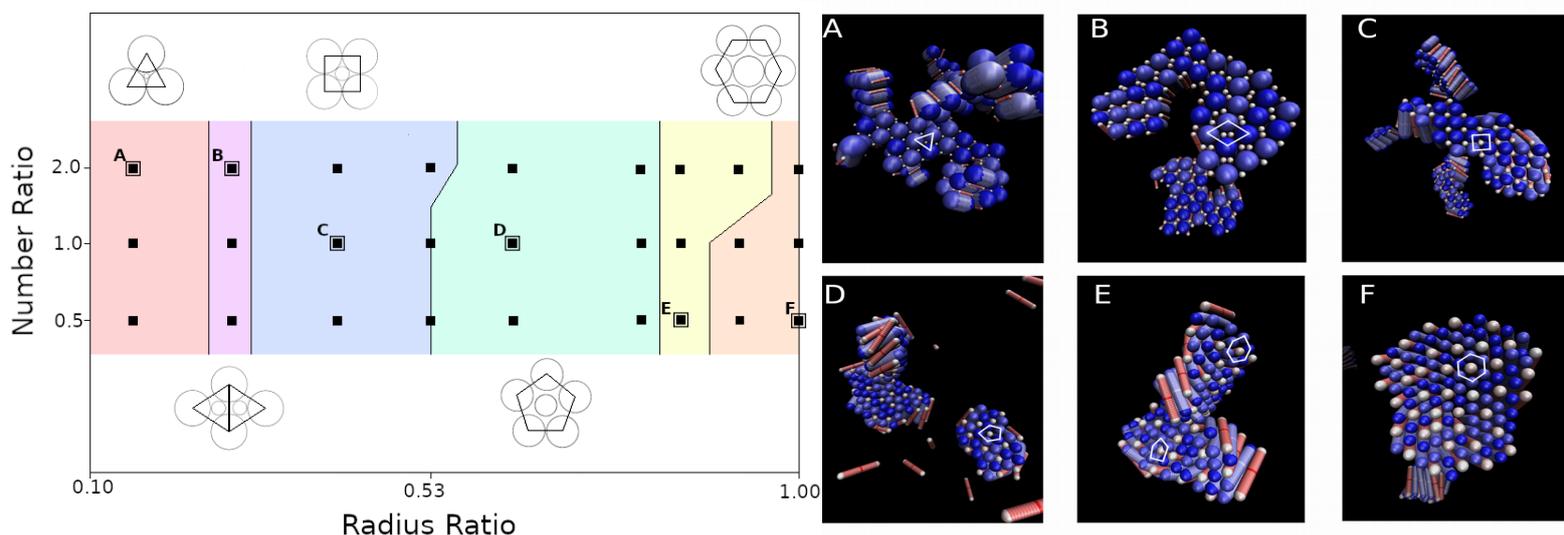
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Formation of Binary Nanorod Superlattices

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Binary nanorod assemblies have the potential to increase the efficiency of Luminescent Solar Concentrators by limiting loss mechanisms.¹ This work characterises the ability of binary mixtures of nanorods to assemble into ordered structures, as a function of the diameter ratio, number ratio and rod-rod interactions. This is done through the use of Brownian dynamics simulations of a coarsegrained model of rods in implicit solvent. We find that a wide range of ordered monolayer structures can be stabilised, including some predicted from hard disc packings as well as novel structures with local pentagonal order.² A combination of attractive and repulsive interactions between the rods is required to prevent aggregation of similar rod types, and using the correct number ratio is found to be important for extended superlattice formation.



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Initial attachment of *Aureobasidium pullulans* conidia on antifungal painted and polyester coated surfaces using Synchrotron sourced macro ATR-FTIR microspectroscopy

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The colonisation of surfaces by environmental fungi in both indoor and outdoor conditions is a common cause for concern, with adverse consequences ranging from damaging the aesthetic appearance of these surfaces or compromising the integrity of the surface, to becoming an source of infection for sensitive (immunocompromised) individuals. In this study, we analysed the initial conidia attachment dynamics of *Aureobasidium pullulans* fungus on polyester-coated and antifungal painted surfaces. A Principal Component Analysis (PCA) was performed on the organic compounds, including carbohydrates, proteins and lipids, that were detected during the initial conidia attachment stage using ATR-IR microspectroscopy. Scanning Electron Microscopy (SEM) was also employed to study the morphology of the conidia and their attachment patterns. It was found that *A. pullulans* conidia were able to initiate a robust attachment to the surfaces after 24 h of contact, most likely due to secretion of extracellular polysaccharides and glycoproteins that may play a major role during the initial attachment of the fungi onto the surfaces. This study also confirmed that ATR-FTIR is a powerful tool for elucidating the chemical compounds involved in fungal adhesion to a surface.

Liquid-phase TEM as a window to bacteria-nanoparticle interactions

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Silver metal nanoparticles have been shown to possess antimicrobial activity, however the precise mechanism for this activity is yet to be observed [1]. In this research, we characterise Ag@SiO₂ nanoparticles for their morphological, chemical, and antimicrobial properties. The particles were first characterised using high-resolution Transmission Electron Microscopy, Scanning Electron Microscopy, and X-ray photoelectron spectroscopy. Antimicrobial activity was determined by UV-Visible assays and liquid-phase TEM of *E. coli* with 6 wt% Ag particles in a porous SiO₂ framework.

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Multivariate UV-Vis analysis of antimicrobial response

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UV-Visible spectra are often used in microbiology to chart the growth of bacteria under various conditions [1]. Typically, the optical density (OD) at the 600 nm wavelength is used as the sole reported value, neglecting chemical data which could be present in the totality of the spectrum. In this research we determine through multivariate analysis of *E. coli*, *S. aureus*, and MRSA [2], if using UV-Vis spectra from 220 nm to 1000 nm can provide additional chemical or biological information regarding the nature of microbial response to antimicrobial agents and the development of antimicrobial resistance.

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The Physical Characterization of novel Aryltrifluoroborate Ionic Liquids

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The physical properties of aryltrifluoroborate alkylammonium salts encompasses their melting point, decomposition temperature, viscosity and phase transitions. These physical properties are important when considering the appropriate salt for industrial or academic applications, e.g. chemical synthesis and positron emission tomography. The relationship between these properties and the structure of the salts anion and cation have only briefly been investigated in the literature and so this study has aimed to combat this lack of knowledge. To catalogue these physical properties in association with their anion, 16 novel aryltrifluoroborate salts with a tetrabutylammonium cation were experimented on using various characterisation techniques. They were found to have melting points around or below 100 °C and so are classified as ionic liquids. The structure-property relationship of these ionic liquids were investigated using the structural isomers of the aryltrifluoroborate anion. With specific attention on the meta and para substitution of fluorine, chlorine, bromine and iodine as functional groups. The results showed the tetrabutylammonium cation to be highly stable compared to the cations previously studied in aryltrifluoroborate literature. It also showed that the isomers of meta and para disubstituted benzene rings follow similar trends to non-ionic molecules with analogous structures that have substituted the trifluoroborate group for a common functional group. This meant that the symmetry formed by a para substitution created better packing efficiency and higher thermal stability. The viscosity trends seen in the literature where high viscosity is caused by greater ion size and increased van der Waals forces was also seen in the sample set of aryltrifluoroborate ionic liquids.

Fabrication and characterization of multifunctional self-healing pectin-based hydrogel and its drug delivery applications

Yue Gao¹, Rico Tabor¹, Harald Janovjak², Boon Mian Teo¹

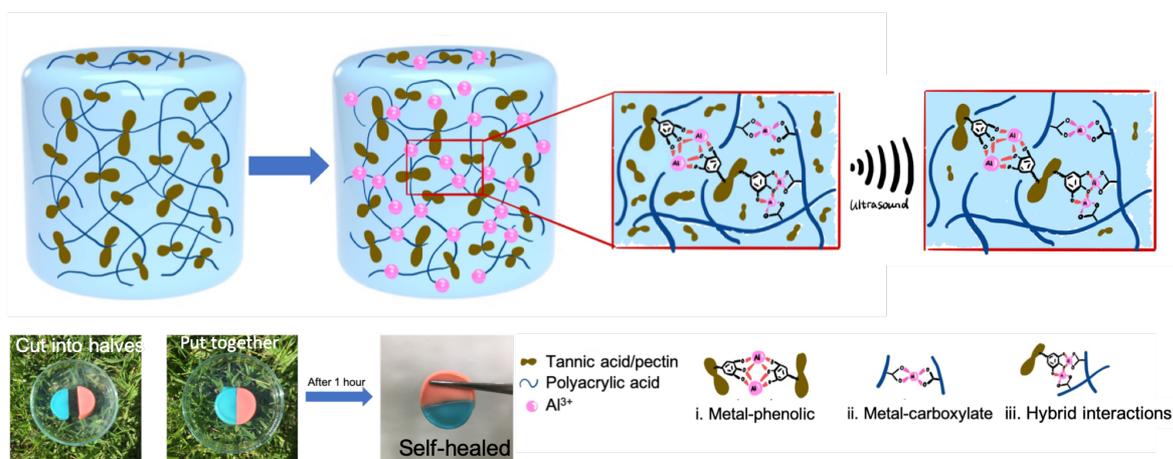
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Despite the emergence of new technologies and the recent extraordinary progress in creating biopolymer-based, self-healing hydrogels, there is still an increasing demand for materials, possessing multifunctionality and better mechanical properties. Commonly, these materials are fabricated by polymerising functional organic monomers to obtain multifunctional hydrogels. These organic components and the resulting hydrogel system, however, are not biocompatible and are non-ideal for biomedical purposes.

In order to solve this issue, we designed a pectin-based hydrogel with interesting properties by constructing a double-network structure from polyacrylic acid (PAA) and introducing tannic acid (TA) as the 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 PAA, which was used to create permanent and dynamic networks, based on ionic interactions and hydrogen bonds. Meanwhile, TA plays a major role in the reversible interactions within the hydrogel network, while acting both as a natural anti-bacterial and anti-inflammatory agent. The inherent biocompatibility of these natural biopolymers, constituting the hydrogel, makes this system an outstanding candidate as a drug delivery platform and for other biomedical applications. The results of this work provide insights in combining and processing nature-derived biopolymers for fabricating new materials to promote the use of sustainable resources and green chemistry.



Cellular Internalization and Uptaking of Different Shapes Colloidal Nanoparticles by HeLa Cells

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In drug delivery applications, particle-based systems have been used widely due to the possibility to precisely alter their physicochemical properties such as size, shape, surface charge to achieve desirable properties in intracellular environment. The way in which nanoparticles enter a biological cell is an important factor in determining their efficacy as drug carriers, biodistribution and toxicity. Most research thus far has focused on the comparison of spherical and rod like particles on cellular internalisation and transport. However, there has been a flurry of papers reporting on single and multiple - cavity shape particles as potential drug carrier.^{1, 2}

Here, we discussed the synthesis of bowl shaped polydopamine (PDA) nanoparticles with precise control in size and shape. Spherical and bowl shaped PDA nanoparticles were incubated with HeLa cells and their internalization behaviors was investigated using a suite of characterizations techniques. We found that bowl shaped PDA nanoparticles adhere to the cells and our results demonstrated significant uptake of bowl shaped nanoparticles compared to the spherical counterparts. These and some other results will be presented. Our results showed the cellular internalization behavior of nanoparticles is shape dependent and such information is crucial to design nanoparticles for biomedical applications.

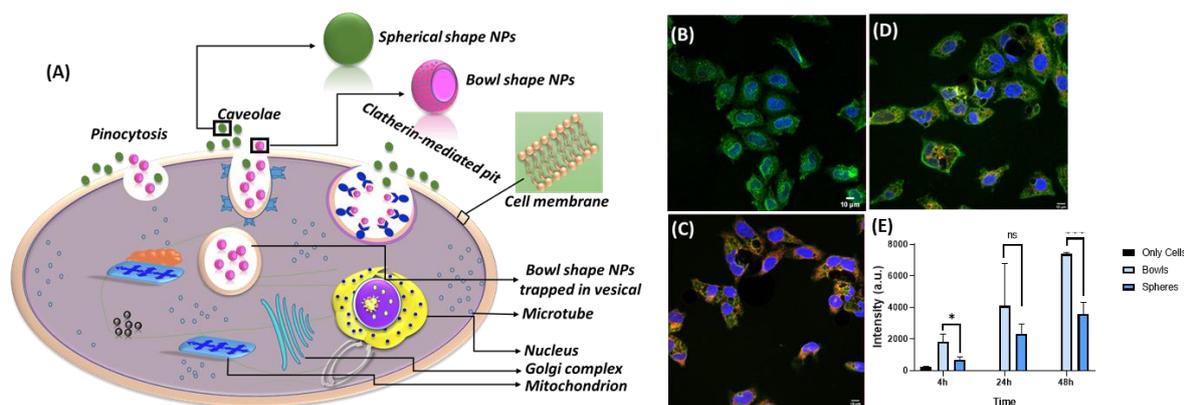


Figure 1. (A) Schematic diagram of cellular internalization of bowl and spherical shape nanoparticles, (B) to (D) confocal images of (B) only HeLa cells, (C) cells after incubation with PDA bowls for 48h and (D) cells after 48h of incubation with PDA spheres, (E) Fluorescence intensity analysis of HeLa cells after incubation with PDA bowls (light blue) and PDA spheres (deep blue) for 4 h, 24 h, 48 h along with the control (black).

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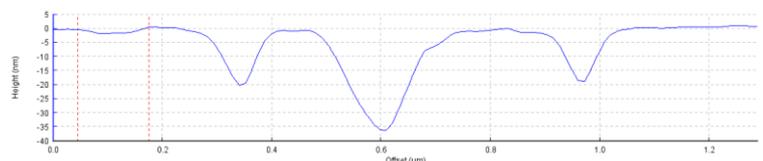
Enhanced dissolution driven by interfacial electric fields between dissimilar surfaces

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As strange and surprising as it may seem, the dissolution rate of certain inorganic material surface such as silica (SiO_2) can be enhanced well above its intrinsic rate by simply pressing it against another surface in an aqueous electrolyte. This phenomenon, known as ‘pressure solution,’ has been well known but poorly understood in the geological community for more than 100 years and yet remains virtually unknown amongst the broader scientific community. Traditionally, the pressure solution phenomenon is explained as an effect of mechanical (i.e. lithostatic) stresses¹ which lowers the activation energy to dissolution by raising the chemical potential energy of stressed bonds within the ‘contact’ junction between the surfaces. The experiments presented in this report challenges this mechanochemical mechanism of pressure solution and instead shows that enhanced dissolution rates are caused by the presence of large interfacial electric fields produced by the surface potential gradient between dissimilarly charged surfaces when pressure pushes them into very close proximity. At very large lithostatic pressures (i.e. GPa), the separation between surfaces collapses to just 3-6 Å corresponding to just 1-2 Stern layers. In this highly confined geometry, the electric fields, emanating from the opposing surfaces is insufficiently screened by counter ions present within the confined water film. Due to the very small separations, even small surface potential gradients on the order of just a few hundred mV can give rise to electric field strengths in excess of 1.0 V/nm. Experiments performed by pressing conductive diamond against silica demonstrate that the dissolution rate can be correlated strongly with the magnitude of the surface potential gradient between surfaces resulting is a relationship resembling electrochemical corrosion—albeit without any obvious electrochemical oxidation/reduction reactions. Likewise, it was found that oscillating the contact pressure at kHz frequencies effectively led to a 2-3 order of magnitude further enhancement in the silica dissolution rate consistent with recently described ‘surface resonance’ effects on catalytic reactions². Our experiments thus lead to a new understanding of pressure solution that sees the phenomenon as an electrocatalytic process through which the autoionization rate of highly confined water is greatly enhanced resulting in accelerated silica dissolution via acid/base reactions. In addition to providing a new understanding of the role of electric fields on chemical reactions, we demonstrate the utility of the pressure solution effect in the area of nanofabrication enabling methods of direct-write and nanoimprint lithography to be performed directly into inorganic substrates.



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Nano-structured surfaces for anisotropic droplets and graphene oxide templating

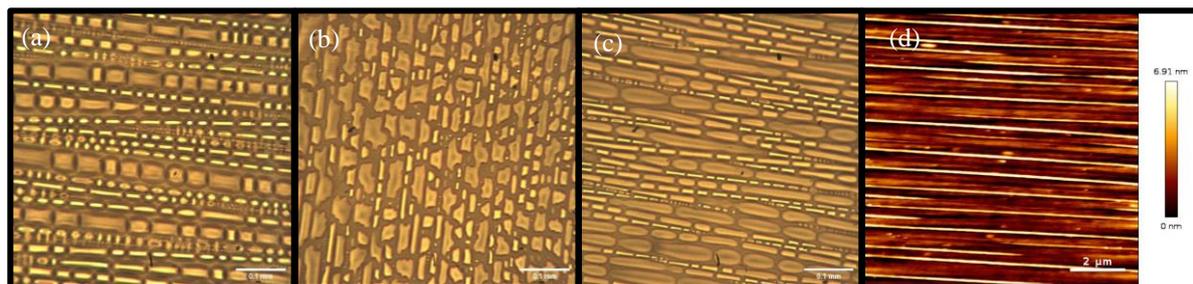
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Poly(dimethylsiloxane) (PDMS) has previously been used to make ordered, wrinkled surfaces at the nanoscale by a process of stretching, oxidising, and relaxing. These highly ordered surfaces have been applied for aligning particles, and inducing anisotropy in water droplets that are placed on the surface.¹ We found for the first time that the formation of hydrophobic cracks parallel to the strain during the wrinkling process led to more significant anisotropy in water droplets due to the added effect of chemical heterogeneity.

Two new treatments of PDMS were developed by changing the order of stretching and oxidation, each of which resulted in the formation of different surface structures such as valleys and ridges due to the changes in strain on the surface. Upon investigation of the wetting properties using a condensation chamber, it was found that these varying structures caused noticeable differences in the anisotropy and directionality of droplets that formed on the surfaces, as shown in the figure below. In each case, droplets generally aligned with the largest hydrophobic feature, and features that were hydrophilic (due to oxidation) had little effect on droplet shape. The strong directional correlation of droplets may allow these surfaces to have applications in microfluidics, water capture, and other nanotechnology applications after further refinements.



In addition to forming anisotropic droplets, structured PDMS was also used to template graphene oxide (GO), and wet-stamp the resulting wrinkled GO films onto glass slides. This gave stripes of GO as seen in panel (d) of the figure above, which were successfully reduced, giving a higher conductivity. This method shows promise in the formation of printable, metal-free, nanoscale electronic structures.

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Unraveling Cellulose-Mucin interactions to comprehend Epidemic Thunderstorm Asthma

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Epidemic Thunderstorm Asthma (ETSA) is triggered by inhalation of air particulate matter including inorganic particles, spores, dust, and airborne pollen grains, which largely affects people regardless of their age, gender, ethnicity etc., within a short span of time.¹ The world's largest ETSA event occurred in Melbourne, Australia in November 2016 which affected thousands and left 9 dead, costing billions of dollars.² Of all air-particulate matter, grass pollen grains are thought to be the leading cause of the ETSA outbreak, having been carried by updrafts from the pasture grass lands of South Eastern region of Australia.³ Pollen is a type of microparticle used by plants for sexual reproduction,⁴ that varies in size and shape depending on its species. Pollen is well-known for causing allergic rhinitis (hay fever) by penetrating the mucosa of tracheal epithelia and lower airways which can lead to the development of asthma. The surface of pollen is comprised of a protective layer (intine), composed of cellulose and hemicellulose, which is hypothesized to initially interact with glycosylated polymers of mucin causing onset of hypersensitive immune reactions. Additionally, pollen grains undergo morphological and surface alterations, such as sintering of cellulose caused by the severe environmental conditions in thunderstorms, including lightning and humidity.

In this poster, we describe the use of a highly sensitive surface analysis technique, the quartz crystal microbalance, to elucidate physicochemical aspects of allergen-causing interactions. We describe our investigations of cellulose-mucin adsorption and our future plans for neutron reflection analysis of the system. These data will be coupled with concomitant immunological research to enable the mechanistic understanding and prevention of ETSA.

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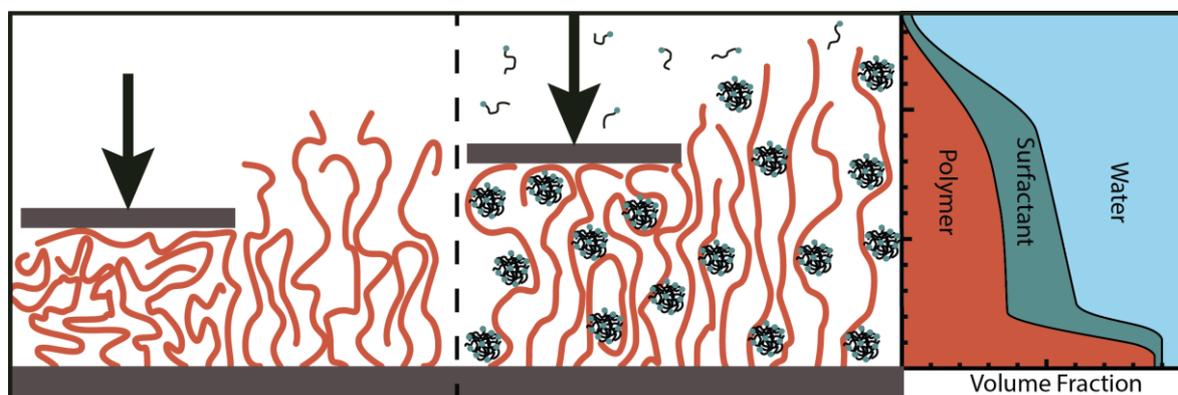
Examining the effects of surfactants on the structural and mechanical properties of a thermoresponsive polymer brush

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Layers of densely tethered polymers (polymer brushes) are of interest due to their unique lubricating and antifouling properties, as well as for the insight into polymer behaviour that their immobilised nature affords. When these brushes are constructed from stimuli-responsive polymers, i.e. the thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM), their structure – and hence their properties – can be modulated via a stimulus-induced conformational change. To enable application the behaviour of these responsive systems in complex environments needs to be understood. Surfactant solutions are one example of a relevant environment, as mixtures of polymers and surfactants are ubiquitous in consumer products.



Here the interactions between a range of surfactants and a PNIPAM brush are explored; a combination of ellipsometry, fixed angle optical reflectometry, neutron reflectometry (NR) and quartz crystal microbalance techniques are used to quantify the polymer nanostructure and the location of the surfactant within the interface. By subjecting the brush to a confining force and measuring its conformation with NR the mechanical implications of the presence of surfactant are also determined. A rich surfactant-specific behaviour is observed and found to be headgroup dependent, consistent with prior work on other PNIPAM architectures. Anionic surfactants swell the brush layer, even at concentrations well below the CMC, as surfactant decorates the neutral PNIPAM with charges, which also aid the layer in resisting mechanical compression. The ability of NR to resolve the concentration profiles of both polymer and surfactant at the interface addresses questions unresolved in current literature.

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Low ppm H₂ gas sensing at room temperature using Pd/TiO₂ based colloidal crystals.

ABSTRACT

Hydrogen (H₂) gas sensors are well in demand and their employment is not just restricted to industrial process control and leak detection applications. For instance, H₂ detection is also required in the food and medical industry to determine the presence of various types of bacteria. Furthermore, detection of low-H₂ concentrations is essential for developing breath analyzers for the non-invasive diagnosis of some gastrointestinal diseases (GID). However, there are major challenges to overcome in order to achieve high sensitivity and hence low limit of detection (LoD) toward H₂. In this study, it is demonstrated that light assisted amperometric gas sensor (AGSs) based on long-ranged ordered crystals (LROCs) of TiO₂ colloids decorated with Pd_x nanoparticles (NPs) as the sensitive layer enables the detection of H₂ gas down to low ppm levels. The sensor response profiles revealed that the sensor's signal to noise ratio (SNR) was higher in the presence of light with 9V bias (relative to other conditions used), producing a LoD of only 3.5 ppm. This sensor performance makes it attractive for applications that require low-level (ppm as opposed to conventional % levels) H₂ gas detection. Most importantly, the developed sensor exhibited high selectivity (>93%) towards H₂ over other gas species commonly found in the environment.

KEYWORDS: light-assisted amperometric sensor; photocatalyst; long-ranged ordered crystals (LROCs); photocatalytic oxidation; hydrogen gas sensing.

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Examining Specific Ion Effects in Glycerol from Concentration Depth Profile using NICISS

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Adsorption or desorption of ions on surface depends upon its solvation shell and change in surface energy caused by dissolution of ion in a solvent[1]. In order to find out overall information about specific ion effects, understanding this information for cation and anion in variety of solvents is important[2]. However, only few articles have tried to provide this information experimentally. Aim of this research is to find out if concentration depth profile relies on interplay of anion-cation, anion/solvent and cation/solvent effects which is done by obtaining depth profile information for each ion in variety of solvents and how this change for each ions and solvents. Also using concentration depth profile, we can obtain information for ionic adsorption or desorption on liquid surfaces and thermodynamic information[3].

Specific Ion trends are investigated in Glycerol with 6 salts (NaCl, NaBr, CsCl, CsBr, LiCl & LiBr) using Neutral Impact Collision Ion Scattering Spectroscopy (NICISS) [4]. Glycerol is a polar solvent with high dipole moment (2.56 D), dielectric constant and very low vapor pressure. As NICISS investigation is done in UHV condition so low vapor pressure & polar solvent nature is the reason of choosing glycerol with further scope in examining similar effects with other polar & non-polar solvents.

Keywords: Specific Ion Effects, Concentration Depth Profile, Liquid Surfaces, Glycerol

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3D printing microfluidic devices to study drop deformation

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Three dimensional (3D) printers are now commonplace in many fabrication applications, yet commercially available printers to produce microfluidic devices are just becoming available. In this work we evaluate the performance of a microfluidic 3D printer, the Dolomite Fluidic Factory. Our goal was to print a T-junction for drop generation and two constrictions for surface tension measurement in a microfluidic device in order to study drop formation and interfacial properties in liquid-liquid system. The designed microfluidic device was fabricated using two 3D printing techniques and then tested in the laboratory. Seven settings of Fluidic Factory were tested and recommendations of each setting were obtained for printing the designed device. The most important settings are addition of skirt and layer offset of -0.1mm, which must be selected together to provide the best visual effect for observing clear drop generation under microscope. In addition, a Standard Operation Procedure (SOP) was developed with ticks and tips for printer users in the future. Oil droplets in water were not generated due to the hydrophobicity of the material used in Fluidic factory and using SDS aqueous solution with a concentration over its CMC turned out to be inappropriate for modifying channel wall from hydrophobic into hydrophilic; further development is required.

The colloidal properties of detonation nanodiamonds in water

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Nanodiamonds have received significant attention from the scientific and engineering communities due to their unique physiochemical properties. These properties are exploited in many applications from drug delivery and biosensing to composite materials and abrasives.¹ Most particles are colloidally stable in water and many organic solvents without the need for stabilising ligand molecules. However, their colloidal properties and aggregation behaviour in simple and controlled aqueous environments remain largely unexplored and poorly understood. We report the dynamic aggregation of detonation nanodiamonds in water.

We demonstrate that charge-stabilised ~5 nm sized primary particles dynamically form elongated, chain-like structures in solution. We employ dynamic light scattering (DLS), small-angle X-ray scattering (SAXS) and cryogenic transmission electron microscopy (cryo-TEM) to show the presence of these structures in water at the nanoscale (TEM) and in ensemble measurements (light and X-ray scattering). We also investigate the effect of particle concentration and ionic strength on the dynamic aggregation behaviour. Our results suggest that the complex surface chemistry of detonation nanodiamonds leads to a unique form of dynamic aggregation and self-assembly in solution, paving the way towards an improved understanding of their colloidal properties and novel applications.

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INVESTIGATING THE BROAD ANTIMICROBIAL PROPERTIES OF FEW-LAYER BLACK PHOSPHOROUS NANOFLOKES

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The continual rise of antibiotic resistance is a major global health epidemic which will affect future generations¹. The decline in effectiveness of conventional therapeutic treatments will have drastic health, economic and societal challenges. To combat this emerging issue the next generation of antimicrobial agents may utilise the unique antimicrobial properties of nanomaterials, including two-dimensional (2D) materials. Recently, there has been significant interest in the use of few-layer black phosphorous (BP) nanoflokes as possible antimicrobial materials. This project investigated the broad-spectrum antimicrobial activity of few-layer BP nanoflokes exfoliated onto a small range of model and medically relevant surfaces. The BP nanoflokes, even in nanogram amounts, showed high antimicrobial activity towards a wide-range of bacteria, including *Escherichia coli*, *Pseudomonas aeruginosa*, methicillin resistant *Staphylococcus aureus*, *Salmonella typhimurium*, and *Bacillus cereus*, as well as the fungal strains, *Candida albicans*, multidrug resistant *Candida auris* and sensitive, Fluconazole-resistant, and Ampicillin-resistant *Cryptococcus neoformans* cells. To establish the viability of BP as an antimicrobial agent, the bio-compatibility with mammalian cells was shown using L929 mouse fibroblasts, which displayed no discernible cytotoxicity. Finally, possible practical applications were assessed by exfoliating the BP onto medically relevant surfaces, such as implant materials. This study establishes the broad antimicrobial activity of few-layer BP nanoflokes and the possible applications for effective treatment and prevention against pathogenic bacteria and fungi infections.

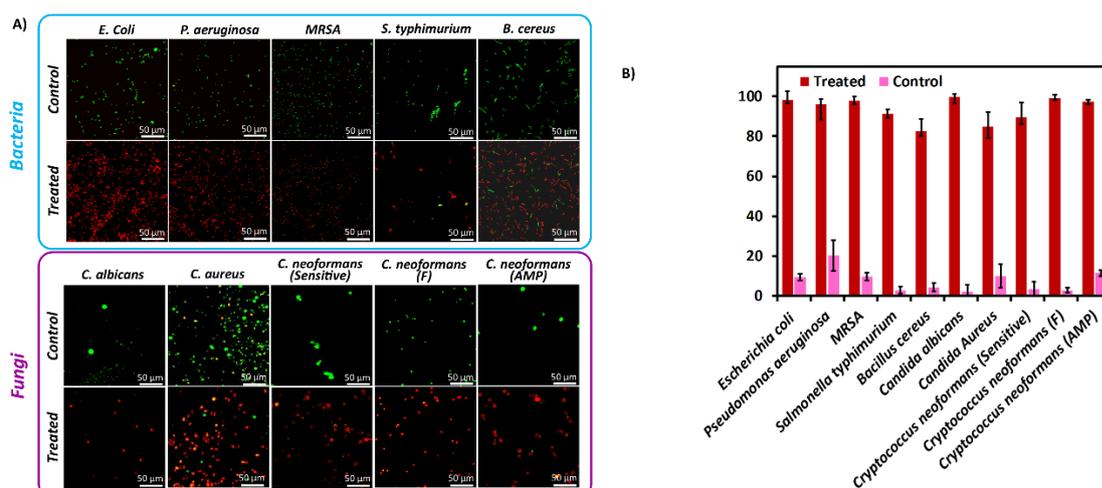


Figure 1. Broad-spectrum antimicrobial activity of few-layer BP. A) Control and Phosphorus treated CLSM images of the bacteria, *E. coli*, *P. aeruginosa*, MRSA, *S. typhimurium*, and *B. cereus*, as well as the fungus *C. albicans*, *C. auris*, *C. neoformans*, *C. neoformans* (F), and *C. neoformans* (AMP). B) Cell viability of the microbial cells incubated in the presence of few-layer BP as quantified from the CLSM images.

Bioinspired Polynorepinephrine Nanoparticles as an efficient vehicle for enhanced drug delivery

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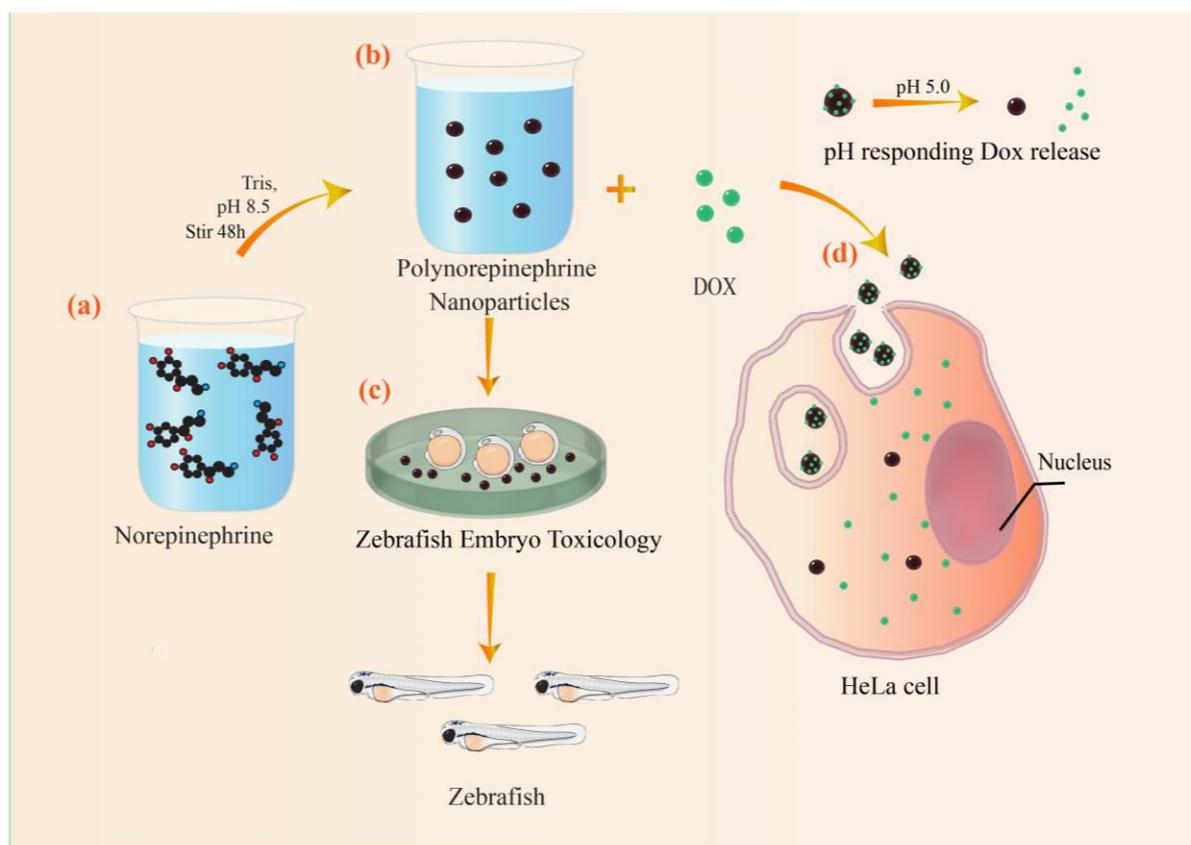
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Novel drug delivery vehicle with excellent biocompatibility, high delivery efficacy is in urgent need for cancer therapy. Herein, polynorepinephrine (PNE) nanoparticles with controllable size modification were fabricated via the autoxidation of norepinephrine monomers in an alkaline water/ethanol mixture via stirring at room temperature. Facile optimization of particle size to enhance particle stability and biocompatibility by varying solvent and monomer dosage was demonstrated both *in vitro* (HeLa cells) and *in vivo* (Zebra fish embryos). After loading the anti-cancer chemotherapy drug doxorubicin (DOX), PNE/DOX could realize a consistent and pH responsive release profile of DOX, resulting in an enhanced pharmaceutical cytotoxicity of DOX on HeLa cells at tumour extracellular microenvironments. Taken together, the PNE nanoparticles represent a new class of melanin particles with promising potential in drug delivery and as a therapeutic platform for cancer treatment.



Linking microstructure to rheology for wormlike micelles using rheoSANS

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Wormlike micelles (WLMs) are elongated, thread-like surfactant aggregates that form spontaneously under certain conditions.¹ At sufficiently high concentrations, WLMs overlap and entangle with each other and this change in microstructure causes a rapid increase in viscoelasticity and zero-shear viscosity.¹ Moreover, it provides significant shear-thinning character, a type of ‘non-Newtonian’ flow behaviour. These properties are very useful in a variety of industries and formulations, including as personal care products, drag reducing agents and fracturing fluids for oil and gas field stimulation.²⁻⁵ Despite their ubiquity, few studies have investigated mild, non-toxic WLMs (like those found in personal care products) at concentrations relevant to industry formulations. Moreover, no model exists that is able to incorporate and link the known microstructural features of WLMs to their bulk rheological properties.

Here, we seek to investigate and link the microstructure and bulk rheology of WLMs formed by cocamidopropyl betaine (CAPB) and sodium laureth sulfate (SLES) surfactants. To do so, we have conducted small-angle neutron scattering (SANS) measurements on CAPB/SLES WLM samples under shear, a technique known as rheoSANS. From this study we have been able to observe shear-induced alignment of WLMs via anisotropy in the 2D scattering pattern and, for the first time, we are attempting to fit full 2D scattering patterns, as shown in Figure 1. This will allow us to quantitatively determine the degree of alignment of WLMs with the direction of shear, as well as other physical parameters within the SANS range including cross-sectional radius and persistence length. By analysis and comparison of these data with bulk rheology, we aim to establish structure-function relationships for predictive and self-consistent modelling of WLM rheology.

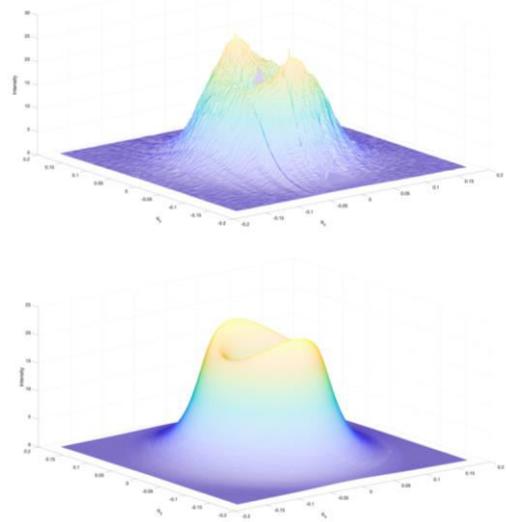


Figure 1 Experimental (top) and simulated (bottom) scattering patterns for 15 wt% CAPB/SLES (66:34) with 2 wt% NaCl at a shear rate of 100 s^{-1} . The height of the plots represents the intensity of scattering.

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The Nucleation Pathway of Self-Assembling Nanorods

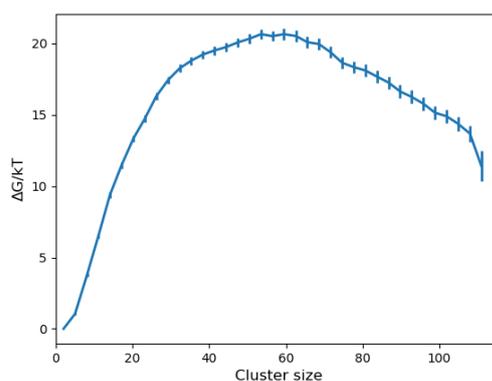
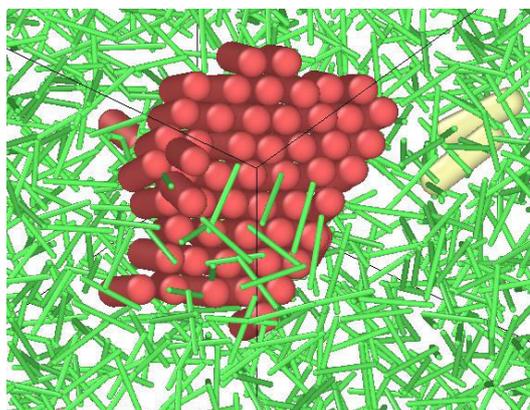
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Nanorods are an interesting material exhibiting both quantum confinement effects, but also having a defined orientation, which can give materials anisotropic behaviour when interacting with light¹. To use these properties, we need be able to control the assemblies that the nanorods form. One common way to assemble nanorods is through the addition of a polymer depletant², that causes the rod/polymer mixture to phase separate, assembling the nanorods into denser, more ordered structures. In these processes, the pathway through which the new phase develops and grows will have a large impact on the uniformity and shape of the final assembly.

We have used Monte-Carlo simulations to look at the nucleation pathway of nanorod assemblies transitioning from an isotropic state to a more ordered state, using umbrella sampling to calculate the free energy change of a growing ordered cluster in the system. From this we are able to view the structure of the growing cluster and determine the favoured growth pathway, whether through a dense amorphous intermediate, a multi-layer cluster, or a monolayer cluster.



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Developing a new SANS model for concentrated worm-like micellar systems.

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The research presented in this work focuses on the modelling of small angle neutron scattering (SANS) data for worm-like micellar systems of sodium laureth sulfate (SLES) and cocamidopropyl betaine (CAPB) in sodium chloride (NaCl) solution. Existing SANS models are able to retrieve architectural parameters of these worm-like micelles (WLMs) for dilute conditions where interactions are minimal, but these models fail at higher concentrations. This work has been centred around modifying the existing flexible cylinder model to incorporate and determine the interactions seen between WLMs at high concentrations ($c \geq 1$ wt%).

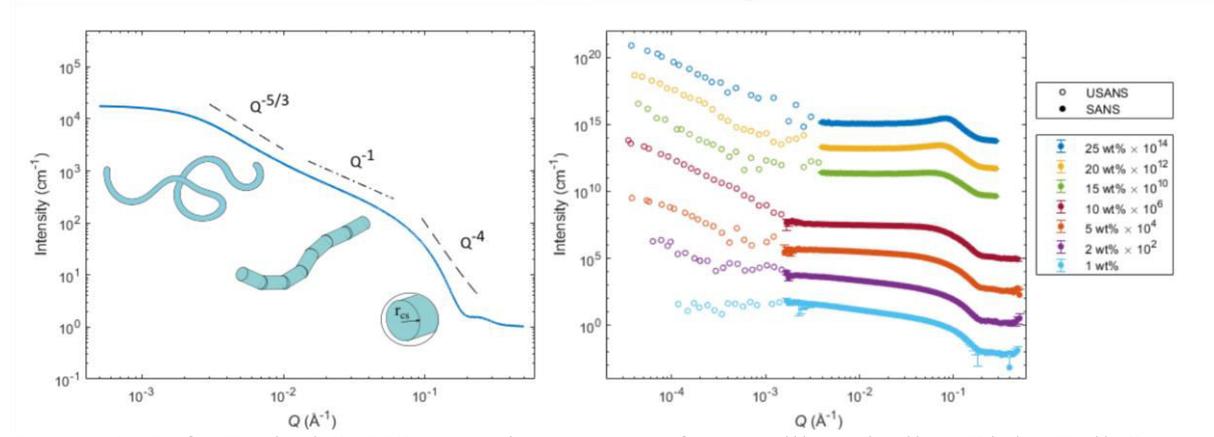


Figure 1: Left: Typical SANS scattering pattern of worm-like micelles. Right: Full Q range (SANS/USANS) of SLES/CAPB (34:66) samples in 2 wt% NaCl. Data is offset by multiplication as indicated.

It was found that charge played a negligible role in the spatial correlations examined in this system and that these correlations could be sufficiently modelled using a *volume exclusion* approach. This work presents a new model for fitting worm-like micellar systems at high concentrations incorporating an approximation for the direct correlation function^{1,2}, $\beta c(Q)$. This model is currently referred to as the polymer reference interaction site model (PRISM), and was successfully able to model samples up to 25 wt% in surfactant concentration. Comparison of the model to experimentally obtained SANS and ultra small angle neutron scattering (USANS) data were used to elucidate the structures of worm-like micelles in concentrated regimes as well as the interactions between them.

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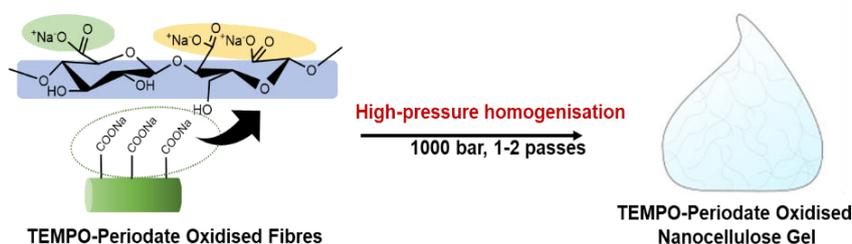
Tuning the Properties of Carboxylated Nanocellulose Gels by TEMPO-Periodate Oxidation

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Carboxylated nanocellulose hydrogels have attracted significant research interest for potential applications in medicine, agriculture, and food packaging. Preparation of these hydrogels are commonly performed by TEMPO-mediated oxidation where anionic carboxylate groups are introduced on the surface of nanocellulose fibres. Our previous studies suggest that the gelation and colloidal stability of TEMPO-oxidised nanocellulose (TOCN) gels are governed by electrostatic interactions and fibre entanglement¹. By varying the fibre dimensions and salt and pH levels, the viscoelastic properties of TOCN gels can vary. However, there is limited information on how the degree of oxidation or degree of substitution affects the properties of carboxylated gels. Recently, we have reported a one-shot TEMPO-periodate carboxylation reaction able to produce carboxylated cellulose with varying degree of carboxylation². In this study, we prepared TEMPO-periodate oxidised nanocellulose (TPOCN) gels with varying degree of carboxylation. The effects of periodate concentration and degree of substitution (DS) on the physical and chemical properties of TPOCN gels were studied. Preliminary results showed that by the introduction of periodate in the classical TEMPO-mediated oxidation, cellulose nanofibers (diameter <20 nm) with relatively higher carboxylated and degree of substitution can be obtained. We also show that TEMPO-periodate oxidation produces more transparent but weaker hydrogels relative to hydrogels prepared by typical TEMPO-mediated oxidation. By varying the degree of carboxylation, the visco-elastic and optical properties of carboxylate nanocellulose gel can be tuned.



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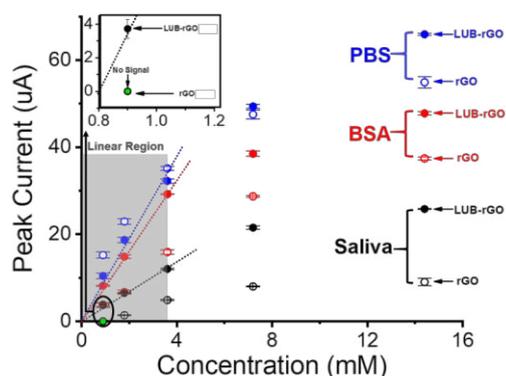
Lubricin: an antifouling coating for carbon-based screen printed electrodes

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Electrochemical biosensing is a widespread technique used for the detection and quantification of target electroactive analytes in biological matrices. Carbon-based screen printed electrodes (SPEs) provide an inexpensive, commercially available and simple to use option for in-situ analysis of bioassays; however, the reliability and accuracy of these carbon electrodes when used for potentiometric sensing is heavily reliant on maintaining a pristine electrode surface free from contamination by non-specifically adsorbed biomolecules. Preventing this surface fouling in bodily fluids such as blood or saliva without likewise compromising the surface electrochemical activity is a major impediment that prevents the wider applications of these carbon electrodes in electrochemical biosensing and point-of-care diagnostics. An effective way to overcome this problem of biofouling is the use of an antifouling surface coating based on lubricin (LUB). LUB is a large glycoprotein found in the articular joints of mammals with the ability to self-assemble on surfaces of different nature, creating an antiadhesive brush layer.[1] Atomic force microscopy and electrochemical experiments were performed using glassy carbon, carbon black SPEs, and reduced graphene oxide SPEs in order to evaluate the antifouling capabilities of LUB coatings in highly fouling biological solutions. The LUB coatings have been shown to exhibit outstanding antiadhesive properties, size selectivity, self-assembly as well as providing excellent electrochemistry in these highly fouling solutions.



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Synthesis of nanodroplets of Liquid Metal labelled with DYES

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The usage of liquid metals (LM) in biosystems is enabled by the fact that Ga³⁺ and In³⁺ ions present very low cytotoxicity¹. Galinstan (LM eutectic alloy of Gallium, Indium, and Tin) droplets combined with iron powder develop a shape transformation under magnetic field. This shape transformation could be used as an anti-biofilm treatment and have numerous application in medical and biomedical area. LM particles under magnetic exposure turn star-shaped and cause a physical disruption of the biofilm of the cell². Particle size control and labelling of these particles with fluorescent markers (DYE) is a major challenge for the desired application. Sonicated liquid metals are reduced in nano and micro size droplets that allow them to be absorbed into cells. Attaching a DYE on the LM surface enable to follow the particle in contact with the cell. The possibility of reducing the size of liquid metals and at the same time functionalising their surface with dyes is a major asset for the development of a new kind of drugs.

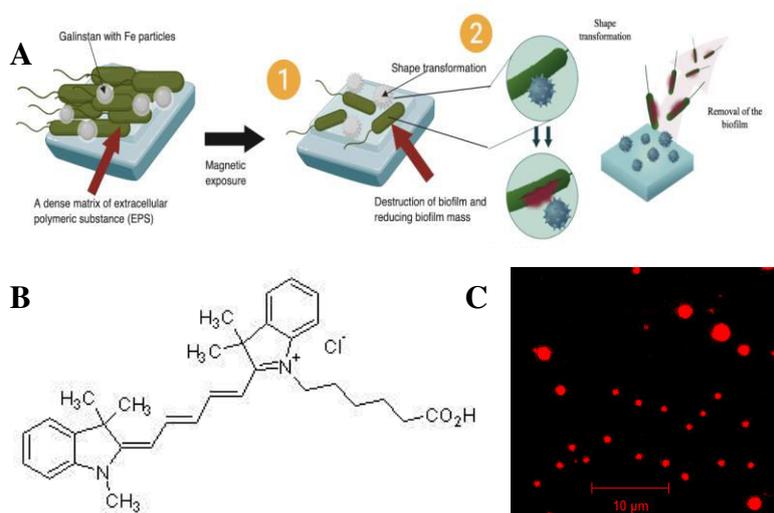


Figure 1. A. Antibacterial activity of nanodroplets LM due to the magnetic exposure. 1) A magnetic field is applied on the LM droplets. 2) Shape transformation, spinning and disruption of the cell's biofilm. B. Chemical structure of the Cyanide 5 carboxylic acid, used as a Dye. C. Fluorescent microscopy imaging of nano-sized and micro sized particles labelled with Cyanide 5 carboxylic acid.

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Ultra-low fouling active surface for bionic implants

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Electroactive surfaces (i.e. electrodes) are a significant component in numerous biomedical applications, such as biosensors and implantable devices used as bionic neural interfaces and/or controlled drug release platforms. The performance and charge transfer efficiency of electrodes however are significantly effected by the fouling of non-specifically adsorbed proteins at their surface which acts both as a passivation layer and an anchoring point for the further attachment of cells. Developing novel protein-resistant coatings is needed to extend the electrode performance of biosensors and bionic devices^{1,2}. Lubricin (LUB; a.k.a. PRG4) is an abundant glycoprotein, synthesized, secreted and deposited in the synovial cavity, presents promising properties for anti-fouling coatings on bionic electrodes including innate biocompatibility, protein and cell adhesion resistance, and the ability to self-assemble into a highly ordered ‘telechelic’ polyer brush with a low grafting density that preseves a high charge transfer efficiency.^{3,4} This work incorporates LUB into an electrochemically grown conductive polypyrrole (PPy) films to achieve electrodes with excellent fouling resistance and high electrochemical activituy. Methods of fabrication are described and electrochemical properties are characterized in both non-fouling and highly fouling solutions of proteins.

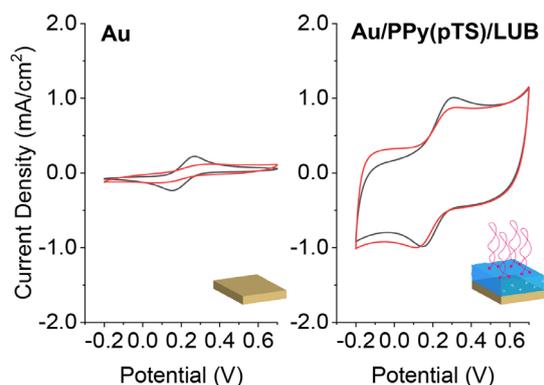


Figure 1: Cyclic voltammograms measured using a scan rate of 100 mV/s and coated gold WE of the oxidation-reduction of a 3.6×10^{-3} mM solution of $K_3[Fe(CN)_6]$ prepared in a nonfouling PBS solution before (black line) and after 2 hours (red line) incubation of BSA protein (5 mg/mL) for a bare gold electrode and a PPy(pTS) and LUB-coated gold electrode. The cycle is the last of 25 cycles.

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Behaviour of Thermoresponsive Polymer Brushes in Mixed Electrolytes

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Specific ion effects relate to any phenomena which depend on the identity of ions present in a system and not merely their valence or concentration.¹ Natural environments are comprised of multi-ion electrolytes, hence, understanding the interplay of different ions is imperative for real world applications. Thermoresponsive polymer brushes are macromolecules which, when end-tethered to a substrate at sufficiently high grafting densities, establish a basis for smart coatings; responding to changes in ambient temperature by altering their physicochemical properties.^{2,3} Polymer brushes from the poly(oligo(ethylene glycol) methacrylate) (POEGMA) family were investigated, which undergo a phase change from well to poorly solvated over a given temperature range (Figure 1a).

Knowledge on the influence of mixed electrolytes on the behaviour of thermoresponsive polymer brushes is limited. The thermoresponse of a POEGMA statistical copolymer brush was monitored as a function of temperature using ellipsometry and neutron reflectometry (Figure 1b-c), in a variety of both pure and mixed electrolytes. In the presence of these mixed electrolytes, the behaviour of the brush was governed by the balance of the influence of ions which can be described as either antagonistic or cooperative.

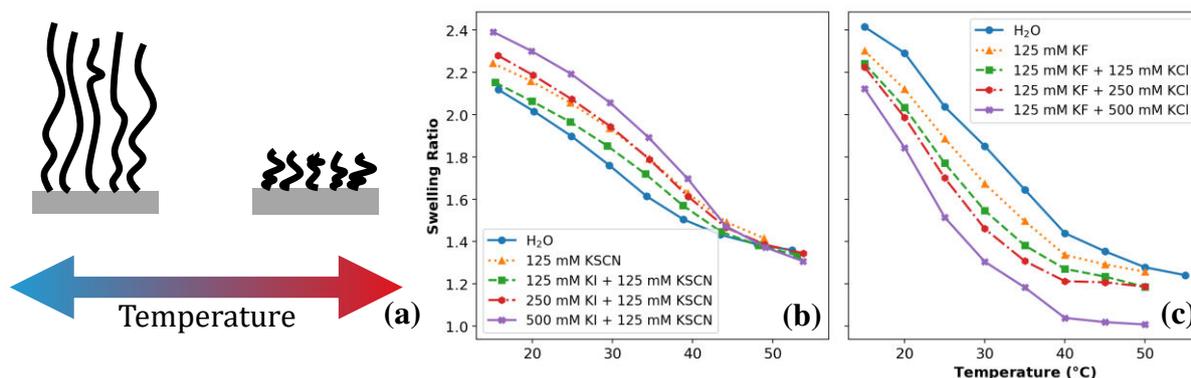


Figure 1. (a) Schematic illustrating the conformation of a thermoresponsive polymer brush as a function of temperature. Ellipsometry data of a POEGMA statistical copolymer brush in pure and mixed electrolytes composed of (b) KSCN and KI and (c) KF and KCl at concentrations of 125 mM, 250 mM and 500 mM.

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