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## **Plenary Speaker Biographies and Abstracts**

## Plenary 1 - Howard Stone

### **Two short stories with interfaces: (1) Thin films, an edge, and a novel similarity solution and (2) Nanoscale capillary instabilities and molecular biology**

#### **Abstract**

I discuss two recent projects combining experiments and theory in different areas of soft matter and fluid dynamics, where interface control the dynamics.

In the first example, we document experimentally the time and (three-dimensional) space variations of the shape of a falling film near the edge of a vertical plate and rationalize the quantitative features using a similarity solution. This example seems unusual since we are able to theoretically show that the shape is described by a nonlinear partial differential equation, involving three independent variables, yet the equation can be reduced by a similarity transformation to a nonlinear ordinary differential equation. The results are in excellent agreement with the experimental measurements. As a second example, we discuss the formation of the spindle in a dividing cell. We report experiments documenting a condensed protein phase on growing microtubules, followed by the Rayleigh-Plateau instability, which produces discrete droplets along a microtubule. We then comment on how the drops drive branching nucleation.

#### **Biography**



Howard Stone is the Donald R. Dixon '69 and Elizabeth W. Dixon Professor in Mechanical and Aerospace Engineering at Princeton University. His research fields include complex fluids, fluid dynamics and chemical engineering, particularly with regards to heat and mass transport problems. His work has impacted phenomena such as surface tension, fluid rotation, viscosity, the motion of suspended particles and microfluidics. Stone's recent research also extends to biological systems, including studies surrounding aerosol transport, bacterial biofilms and microtubules. Dr. Stone received his Ph.D. in chemical engineering from the California Institute of Technology in 1988 and in 1989 joined the faculty of the School of Engineering and Applied Sciences at Harvard University; there he became the Vicky Joseph Professor of

Engineering and Applied mathematics. Dr. Stone was the first recipient of the prestigious Batchelor Prize in 2008 for best research in fluid mechanics in the last decade, and in 2016 he was awarded the Fluid dynamics Prize by the American Physical Society for his "seminal contributions to our understanding of low Reynolds number flows, microfluidics, interfacial phenomena, and biological fluid dynamics, and for his inspirational contributions to teaching and communicating the beauty and power of fluid mechanics, physics and engineering."

## Plenary 2 - Monica Olvera de la Cruz

### Colloidal assembly leading to metallicity

Monica Olvera de la Cruz, Northwestern University, m-olvera@northwestern.edu

#### Abstract

Numerous colloidal crystals have been designed and devised using functionalizing nanoparticles following design rules akin to atomic crystals, where individual colloids behave as atom equivalents (AEs) in lattices. We will review techniques used to achieve single colloidal crystals by exploiting the properties of electrolytes at high salt concentrations and DNA functionalization. We will also describe AEs that behave as electron-equivalents (EEs) when their sizes and grafting density are sufficiently reduced. In mixtures of EEs and AEs, at elevated temperatures the EEs roam within the crystal while also holding the large AEs in specific lattices sites, akin to electron clouds in atomic metals. Additionally, as the temperature decreases, the EEs localize forming compounds. This EE-AE duality produces metallic, intermetallic and compound phases including Frank-Kasper phases. We will describe such localized to delocalized states in different colloidal assemblies, including disparity in charge and size mixtures of oppositely charged particles via a process that resembles sublattice melting in atomic superionics.

#### Biography



Monica Olvera de la Cruz is the Lawyer Taylor Professor of Materials Science and Engineering; Professor of Chemistry; Professor of Chemical and Biological Engineering; Professor of Physics and Astronomy; Director of the Center for Computation and Theory of Soft Materials; and Deputy-Director of the Center for Bio-Inspired Energy Science.

Research by the Olvera de la Cruz group is centered around the development of models to describe the self-assembly of heterogeneous molecules including amphiphiles, copolymers and synthetic and biological polyelectrolytes, as well as the segregation and interface adsorption in multicomponent complex fluids.

She is a member of the American Philosophical Society, the National Academy of Science (NAS), the American Academy of Arts and Sciences and an American Physical Society (APS) Fellow. She was the recipient of various awards and prizes including the 2017 APS Polymer Physics Prize, the 2010 National Security Science and Engineering Faculty Fellowship, the 2007 Cozzarelli Prize (NAS), a Presidential Young Investigator Award of the National Science Foundation (NSF), an Alfred P. Sloan Fellowship and a David and Lucile Packard Fellowship in Science and

Engineering. She is a member of the US Department of Energy's Basic Energy Sciences Advisory Committee. She has served on the editorial boards of numerous peer-review journals and is a Senior Editor for the ACS Central Science.

## Plenary 3 - Wilson Poon

### Soft matter physics and the COVID-19 pandemic

#### Abstract

Much of the science underpinning the global response to the COVID-19 pandemic lies in the soft matter domain. Coronaviruses are composite particles with a core of nucleic acids complexed to proteins surrounded by a protein-studded lipid bilayer shell. A dominant route for transmission is via air-borne aerosols and droplets. Viral interaction with polymeric body fluids, particularly mucus, and cell membranes controls their infectivity, while their interaction with skin and artificial surfaces underpins cleaning and disinfection and the efficacy of masks and other personal protective equipment. The global response to COVID-19 has highlighted gaps in the soft matter knowledge base. I will survey these gaps, especially as pertaining to the transmission of the disease, and suggest questions that can (and need to) be tackled, both in response to COVID-19 and to better prepare for future viral pandemics.

#### Biography



Wilson Poon holds the Chair of Natural Philosophy in the University of Edinburgh, where he conducts research into soft matter and biophysics, with current focus on the rheology of non-Brownian suspensions and bacterial physics. Much of his recent research is inspired by practical applications — from the flow of molten chocolate to microbial biofouling, which he explores via the Edinburgh Complex Fluids Partnership (ECFP).

## Plenary 4 - Jennifer Lewis

### Printing Soft Matter in Three Dimensions

Jennifer A. Lewis

Hansjörg Wyss Professor of Biologically Inspired Engineering

John A. Paulson School of Engineering and Applied Sciences & Wyss Institute  
Harvard University

#### Abstract

3D printing enables one to rapidly design and fabricate materials in arbitrary shapes on demand. I will introduce the fundamental principles that underpin 3D printing methods pioneered by our group. I will then describe the design, composition, and rheological properties of colloidal gels, foams, and polymeric inks that we have developed, which are vastly expanding the capabilities of 3D printing. Finally, I will highlight several examples from our recent work, including the fabrication and characterization of colloidal foams, shape-shifting architectures, and soft functional devices.

#### Biography



Jennifer A. Lewis is the Jianming Yu Professor of Arts and Sciences, the Wyss Professor for Biologically Inspired Engineering in the Paulson School of Engineering and Applied Sciences, and a core faculty member of the Wyss Institute at Harvard University. Her research focuses on 3D printing of functional, structural, and biological materials that emulate natural systems. Prior to joining Harvard, Lewis was a faculty member in the Materials Science and Engineering Department at the University of Illinois at Urbana-Champaign, where she served as the Director of the Materials Research Laboratory. Currently, she directs the Harvard Materials Research

Science and Engineering Center (MRSEC) and serves on the NSF Mathematical and Physical Sciences Advisory Committee.

Lewis has received numerous awards, including the Presidential Faculty Fellow Award, the American Chemical Society Langmuir Lecture Award, the Materials Research Society Medal Award, the American Ceramic Society Sosman and Roy Lecture Awards, and the Lush Science Prize. She is an elected member of the National Academy of Sciences, National Academy of Engineering, National Academy of Inventors, and the American Academy of Arts and Sciences. To date, she has co-founded two companies, Voxel8 Inc. and Electroninks, that are commercializing technology from her lab.

# Adelaide

10/2/21

## **Adelaide – Keynote Abstracts**

## Flotation Puzzles- Encounters, Kinetics and Hydrophobicity

John Ralston, Dr.h.c. Abo Akademi, Finland; PhD Melbourne; DIC Imperial College London; MSc Melbourne ; BSc(Hons) Melbourne; DipEd Melbourne

### Biography



John is a Physical and Colloid Chemist with complementary training in metallurgy, whose research interests embrace various aspects of interfacial science and engineering. In 1994, the Ian Wark Research Institute (1994 to 2015) was founded at the University of South Australia, with John as its Director, until his retirement in 2012. John's research deals with three main themes - how bubbles contact particles; why things stick together and how liquids spread

over surfaces. The problems addressed cross the boundaries from pure physical chemistry to materials science to chemical and minerals engineering, with many connections with, and knowledge transfer to, national and international industry. John has received numerous national and international awards and honours over the years. These include the Chemeca Medal in 2006 [Australia's highest honour in Chemical Engineering], the ATSE Clunies Ross Lifetime Contribution Award in 2009 and the Staudinger Durrer Lecture and Medal in 2012 from the Swiss Federal Institute of Technology, ETH Zurich, for influential contributions to the fields of colloid and surface science. In 2008 John was made an Officer of the Order of Australia. In 2007 he was awarded South Australian of the Year, the first scientist to be so honoured, as well as South Australian Scientist of the Year.

During his research career, John has been awarded over \$200M in competitive grant funding from the Australian Research Council, national and international granting agencies and private industry. His research efforts with his colleagues have returned over \$1.5BAUD to national and international industry with, in the case of minerals research, a verified ratio of 20 to 1 benefit to industry for each research dollar invested. John has actively supervised eighty-five PhD research students. These students have gone on to establish careers in universities, industry and other research institutions throughout the world.

Apart from mentoring research teams at UniSA, his present activities include strong interactions with universities, companies and research institutes internationally. John has an h-index of 72 and his publications have been cited more than 17000 times.

## **Abstract**

The selective capture of specific particles by bubbles is fundamental in mineral flotation. For successful bubble-particle capture to take place the complementary steps of collision, attachment and stability of the three phase contact must be included in any description. How do we describe the selective interaction of single bubbles with specific particles in simple systems and then selective multiple bubble particle encounters or “coagulation” in a many-body heterogeneous environment? Fluid dynamics, physics, chemistry and engineering are all involved. What are the major issues and challenges?

Hydrophobicity is central to flotation, but can be interpreted in different ways, often incorrectly. Bubbles have surfaces which may be mobile, immobile or somewhere in between. Water structure at interfaces is very important. Particle surfaces may be rough at various length scales; are often patchy in terms of chemical and mineralogical composition; are frequently coated with tiny ‘particles’ to varying degrees; and rarely adsorb reagents uniformly. Many minerals comprise faces and edges whose structure and composition differ, along with their dielectric constants, and thus respond to chemical species differently. The aqueous phase may be highly saline. Determining particle separation and fluid mechanical behaviour in opaque, multiphase systems with complex interfaces is therefore challenging. Whilst great progress has been made, major puzzles remain to be solved.

## **Emulsions under Arrest!**

Abigail Thiel, Prerna Dahiya, Syeda Muin, Maryam Hosseini, and Patrick T. Spicer\*  
School of Chemical Engineering, UNSW Sydney

Patrick Spicer

### **Biography**

Patrick Spicer is an Associate Professor in UNSW's School of Chemical Engineering where he leads the Complex Fluids group. The CFG combines microscopy and rheology studies to understand and design smart fluids with unique response and flow behaviour. Pat developed and teaches the core technology and design courses of UNSW's new Chemical Product Engineering stream in collaboration with industrial colleagues. Before UNSW, Pat ran a central engineering research department for the Procter & Gamble Company in the US for 15 years. His group developed new product and process technology there for all of P&G's billion-dollar brands.

### **Abstract**

The combination of two or more emulsion droplets into a single volume is termed coalescence, a process with a strong impact on stability of diverse products like shampoos, explosives, and foods. In some cases, emulsion droplets contain solid or crystalline particles that alter their rheology and response to coalescence. Past observations of microstructure in milkfat emulsions identified structures formed by interrupted or arrested coalescence, resulting in droplet aggregates that are a critical part of food microstructure and texture. Using direct microscopic studies of arrest, we developed a physical model of the process that predicts its extent as a function of droplet rheology and interfacial tension. The experiments also identified a new mechanism of microstructure formation: a restructuring of colliding droplets into denser packings than would be achieved by random, fractal ordering. As this past work is based on studies of only a few droplets at a time, we are focused on validating the models for more realistic populations of emulsion droplets. Microscopy of thousands of droplets forming arrested coalesced structures shows unique structure formation that is consistent with a theoretical model of the restructuring mechanism. We build on this work to include three-dimensional imaging of arrested structures and consider the effects of shear stress and more complex crystalline species on the phenomenon. Droplet arrest and restructuring is then related to product performance measures like rheology and aesthetic texture.

## **Adelaide – Oral Presentation Abstracts**

## **Incorporation and antimicrobial activity of nisin Z within carrageenan/chitosan multilayers**

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An antimicrobial peptide, nisin Z, was embedded within polyelectrolyte multilayers (PEMs) composed of natural polysaccharides in order to explore the potential of forming a multilayer with antimicrobial properties. Using attenuated total reflection Fourier transform infrared spectroscopy (ATR FTIR), the formation of carrageenan/chitosan multilayers and the inclusion of nisin Z in two different configurations was investigated. Approximately  $0.92 \mu\text{g}\cdot\text{cm}^{-2}$  nisin Z was contained within a 4.5 bilayer film. The antimicrobial properties of these films were also investigated. The peptide containing films were able to kill over 90 % and 99 % of planktonic and biofilm cells, respectively, against *Staphylococcus aureus* and methicillin-resistant *Staphylococcus aureus* (MRSA) strains compared to control films. Additionally, surface topography and wettability studies using atomic force microscopy (AFM) and the captive bubble technique revealed that surface roughness and hydrophobicity was similar for both nisin containing multilayers. This suggests that the antimicrobial efficacy of the peptide is unaffected by its location within the multilayer. Overall, these results demonstrate the potential to embed and protect natural antimicrobials within a multilayer to create functionalised coatings that may be desired by industry, such as in the food, biomaterials, and pharmaceutical industry sectors.

† *These authors contributed equally as primary authors of this work*

# Anticancer efficacy of Cyclodextrin-based Nanoparticles containing Alpha-mangostin

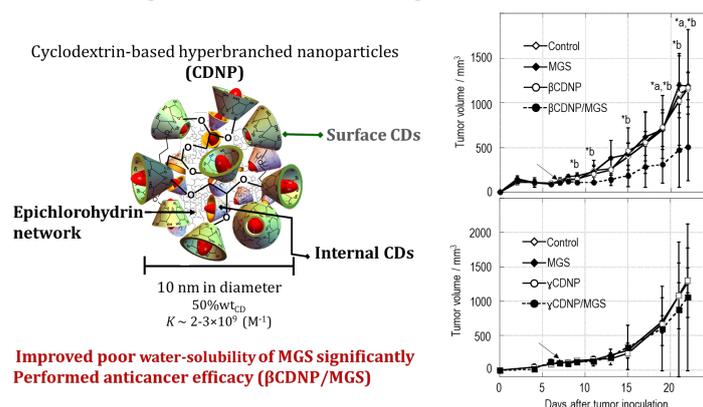
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Alpha mangostin (MGS) is a natural xanthone compound and extracted from mangosteen pericarps. Although MGS has great potential to be an excellent anticancer agent, its extremely low solubility in water seriously impedes its medical application. Previously, we found that cyclodextrin (CD)-based hyperbranched polymer nanoparticles (CDNPs) solubilizes MGS by encapsulating it into the CD cavity and their binding constants became almost 100 times higher than native CDs.<sup>1,2</sup> Our finding suggested that CDNPs could become a good carrier of MGS.<sup>1</sup> In present study, we prepared three types of CDNPs from  $\alpha$ -,  $\beta$ -, and  $\gamma$ - CDs and compared them in terms of the MGS release, and *in vivo* anticancer efficacy.

Firstly, drug release profile showed that all data points of CDNPs/MGS were fitted by bi-exponential first-order equation and performed two steps release: the initial rapid and second slow releases. It suggests a model in which slow and rapid modes are connected in series and, before release, MGS must shift from the slow to the rapid mode. We also assumed that the slow and rapid modes are related to the interior and surface CDs of CDNPs. Based on fitting result, MGS released more gradually from  $\beta$ CDNP/MGS than other CDNPs in the slow mode. Additionally,  $\beta$ CDNP/MGS demonstrated the greatest anticancer efficacy, while no efficacy was observed for the others *in vivo* experiment. On the connection between drug release behavior and anticancer efficacy, we proposed the releasing time in the slow mode is essential for MGS retention until reaching the cancerous region.



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# Evaporation-Driven Flow in Micropillar Arrays: Transport Dynamics and Chemical Analysis under Varied Sample and Ambient Conditions

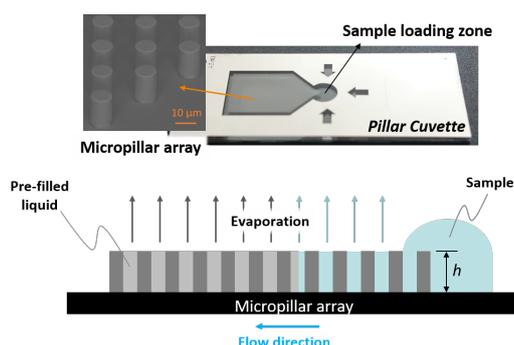
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Microfluidic flow in lab-on-a-chip devices is typically very sensitive to the variable physical properties of complex samples, e.g., biological fluids. In this study, we report evaporation-driven fluid transport (transpiration) in a micropillar array configuration that is insensitive to interfacial tension, salinity, and viscosity over a wide range. The micropillar array (“pillar cuvette”<sup>1</sup>) was preloaded by wicking a known volatile fluid (water) and then adding a microliter sample of salt, surfactant, sugar, or saliva solution to the loading zone. As the preloaded fluid evaporates, the sample is reliably drawn from a reservoir through the pillar array at a rate defined by the evaporation of the preloaded fluid (typically nL/s). Including a reagent in the preloaded fluid allows photometric reactions to take place at the boundary between the two fluids. In this configuration, a photometric signal enhancement is observed and chemical analysis is independent of both humidity and temperature.<sup>2</sup> The ability to reliably transport and sense an analyte in microliter volumes without concern over salt, surfactant, viscosity (in part), humidity, and temperature is a remarkable advantage for analytical purposes.



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2. M.K. Orlowska, B. Guan, R. Sedev, Y. Morikawa, K. Suu, C. Priest, Evaporation-Driven Flow in Micropillar Arrays: Transport Dynamics and Chemical Analysis under Varied Sample and Ambient Conditions, *Analytical Chemistry* **92**(24) (2020) 16043–16050.

# Characterisation of the properties and structure of Poly(N-isopropylacrylamide) layers on silica in alcohols and binary solvents

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Poly(N-isopropylacrylamide) (PNIPAM), a typical thermoresponsive polymer, is not only responsive to temperature but also to the conditions of solutions, such as the presence of salts. Therefore, solids onto which PNIPAM chains have been grafted could be applicable to a wide variety of industrial fields that utilise these properties. In this study, the structural changes of PNIPAM chains grafted onto solid plates were investigated in alcohols and their mixtures with water, using an atomic force microscope (AFM).

AFM imaging (Fig. 1) of the PNIPAM-grafted silica substrate in ethanol-water mixtures showed that the grafted PNIPAM chains exhibited a mushroom-like morphology in mixtures with 20–40 vol.% of ethanol, whereas they exhibited a brush-like morphology in both water and ethanol. Interaction force measurements conducted between the AFM tip and the substrate indicated that the PNIPAM chains exhibited complex expanding-shrinking behaviour, depending on the concentration of ethanol. The grafted PNIPAM chains also expanded with the increase in the carbon number of the alcohol used. Such structural changes are likely to have been caused by the balance of the interchain repulsion, due to the hydration of amides, and the hydrophobic attraction between hydrocarbons in the chains.

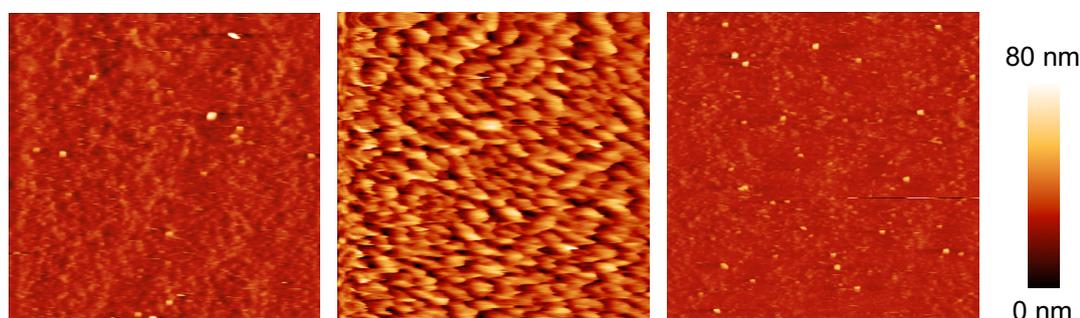


Fig. 1 AFM images ( $5.0 \times 5.0 \mu\text{m}^2$ ) of a PNIPAM layer grafted on a silicon wafer obtained in water (left), water 80 vol% - ethanol 20 vol% mixture (centre) and ethanol (right).

# Adsorption of Inorganic Ions at Liquid Surfaces – Ion Specific Effects

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Adsorption or desorption of inorganic ions at solvent surfaces has relevance in complex biological process, physiochemical systems and as a model system for atmospheric chemistry studies i.e., ionic presence in aerosol droplets influences Cl<sub>2</sub> and Br<sub>2</sub> uptakes. Since the recent developments in surface-sensitive experimental techniques, many investigations have shown that adsorption or desorption of ions in aqueous solution follows specific ion series (direct or indirect Hofmeister series) and this behaviour is believed to be originated from ion-solvent interaction<sup>[1]</sup>. The recent discovery of specific ion effect in non-aqueous solutions suggests that water is not a special liquid in the matter of specific ion effects<sup>[2]</sup>. But, consensus for adsorption or desorption of inorganic ions in liquids other than water is limited hence a clear origination of specific ion effect is not understood. Therefore, to further unravel the origination of specific ion effect at liquid surfaces, we have employed neutral impact collision ion scattering spectroscopy<sup>[3]</sup> (NICISS) to obtain concentration depth profiles of various ions in glycerol and formamide solutions.

Overall, 12 inorganic salts (LiCl, LiBr, LiI, NaCl, NaBr, NaI, KF, KBr, KI, CsF, CsCl & CsBr) dissolved in glycerol and formamide are investigated to compare the depth profile onsets of 3 different ionic subsets: i) anionic depth profiles without varying the cation, ii) anionic depth profiles when paired with varying cation & iii) cationic depth profiles while varying the counter anions. Preliminary results show that ions are driven towards air-liquid interface not only based on their ionic sizes and polarizability but also depending upon the solvent's polarizability. These implications are made from the findings that smaller anions in glycerol are adsorbed closer to the solvent surface in comparison to bigger anions and that cation specific effect is absent from glycerol solution surfaces which is opposite of the results reported so far for ions at aqueous solution surfaces<sup>[4]</sup>.

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# The Effect of Stabilisers on the Interfacial Crystallisation of Lipids

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Crystallisation of lipids at the oil-water interface has a significant effect on the stability of emulsion systems [1, 2]. Interfacial crystallisation is of particular importance to the dairy industry, as interfacial crystals also play an important role in the structure and texture of dairy products. The presence of either included or indigenous stabilisers are also vital to ensure the stability of emulsions during product formation. The effect of these stabilisers on the formation and structure of lipid crystals at the oil-water interface is an area which is of great importance; however, isolating the interface is difficult to achieve by studying emulsion systems.

In this study, a different approach has been taken to study interfacial crystallisation, whereby a single oil-water interface was examined using Synchrotron Small and Wide-Angle X-ray Scattering (SAXS/WAXS) and Profile Analysis Tensiometry (PAT) in the presence and absence of emulsion stabilisers. X-ray scattering provided insights on the influence of stabilisers regarding crystal concentration and structure at the oil-water interface compared to the bulk oil phase, while PAT was used to monitor of the kinetics of interfacial tension in response to surface-active lipid crystal formation. The combination of these two techniques allows for a more detailed study of the oil-water interface and the effect of stabilisers on interfacial crystallisation compared to emulsion systems.

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# high loaded Gold cluster deposited onto the functionalized mesoporous TiO<sub>2</sub>: Efficient photocatalytic methyl orange degradation

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Since water splitting photo catalytically on the electrodes made of TiO<sub>2</sub> single crystals was discovered by Fujishima and Honda<sup>1</sup>, use of TiO<sub>2</sub> semiconductors has been strongly emphasized in various practical applications owing to its unique electronic and optical features; good chemical and thermal stability; and low toxicity and cost<sup>2,3</sup>. However, a wide range of approaches has been ever conducted to increase the TiO<sub>2</sub> photocatalytic activity. It can be achieved by two kinds of modification; 1- Morphological ones included increasing the porosity and surface area; as a result, mesoporous TiO<sub>2</sub> (MTiO<sub>2</sub>) have attracted much attention in versatile fields such as solar fuels and water treatment process, 2- Chemical ones; such as incorporating additional components in the structure of TiO<sub>2</sub> to enhance the sensitivity of TiO<sub>2</sub> towards the visible light region, inhibit the recombination of the photogenerated electron-hole pairs or/and increase the active sites enhancing the photocatalytic activity. In the case of noble metals loaded onto the semiconductor particles, if the size is reduced, it leads to a remarkable improvement in the catalytic efficiency due to two effects: scalable effects and quantum confinement effects.

Gold nanoclusters (NCs) are smaller in size than Au nanoparticles used to modify surface properties. For this reason, the number of atoms forming an Au NC strongly influences the catalytic properties of cluster-modified surfaces. Agglomeration of NCs leads to an increase in NC size, eventually forming NPs, and should be avoided.

MTiO<sub>2</sub> semiconductor application with remarkable surface defects, high surface area, and extensive 3D pore network can help prevent agglomeration of gold clusters. Also, to have stronger interaction between Au NCs and semiconductor surface leading to decreased agglomeration and increasing the loading of the Au NCs, the functionalizing reagent is used to make a system with a high number of active sites to obtain highly active photocatalytic systems.

**Keywords:** Gold nanoclusters, Mesoporous TiO<sub>2</sub>, Photocatalytic activity

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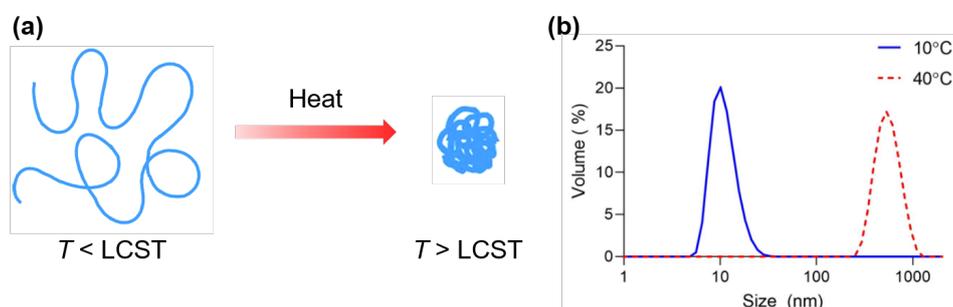
# Thermoresponsive polysaccharides with tunable thermoresponsive properties

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Over the last few decades, there has been a growing interest in polysaccharides (PS) that exhibit thermoresponsive properties and their applications. Whilst some PS are naturally thermoresponsive, their transition temperatures are often too high and not easily tuned. Thus, polymers with a lower critical solution temperature (LCST) are favoured over those with an upper-critical solution temperature (UCST), as they are a solution at ambient temperature and phase transition upon heating<sup>1</sup> (**Figure 1a**). PS with a LCST can only be achieved via synthetic modification of PS, and whilst this has been previously studied, many modified PS have a LCST that is either too high or cannot be tuned. Therefore, in this study we aimed to develop a thermoresponsive PS with a tunable LCST via the functionalisation of dextran with alkylamide groups. We prepared a library of alkylamide functionalised PS using a series of four different amic acids at a range of degrees of substitution (DS). UV-Vis spectroscopy was used to determine the LCST and it was found that the LCST could be tuned by altering the DS, with a higher DS resulting in a lower LCST, and vice versa. It was observed that when heated above the LCST, the functionalised PS transitioned from a solution to a colloidal suspension of aggregated PS globules (**Figure 1a and b**). An *in vivo* toxicity study in mice using one of the thermoresponsive alkylamide functionalised dextrans found no observable difference between the control and formulation treated groups, suggesting that the polymer is biocompatible. Furthermore, preliminary studies on the potential of these PS for use as biodegradable drug delivery systems was investigated through enzymatic degradation and *in vitro* drug release studies.



**Figure 1:** (a) The coil-to-globule transition resulting in the formation of a colloidal suspension. (b) The particle size distribution of functionalised dextrans above and below the LCST.

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## **Impact of bubble size on terminal velocity in water and frother solutions as indicator of surface mobility**

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The bubble rise velocity in liquids is determined by the liquid-air interface boundary conditions. Bubbles having fully mobile surface rise with highest velocity, while tangential immobility at bubble surface cause decrease in the rise velocity. The bubble surface immobilization occurs in the presence of trace amounts of surface active molecules<sup>1</sup>.

The available literature data on air bubble rise in high purity water does not provide unambiguous conclusions regarding mobility of the bubble surface. The biggest discrepancies concern very small bubbles, which may exhibit completely immobile boundary conditions according to Stokes law or have fully mobile water-air interface in accordance with Hadamard-Rybczynski model<sup>2,3</sup>. Results present the systematic investigation on air bubble rise velocity in high purity water for a wide range of bubbles diameters (50  $\mu\text{m}$  – 1.5mm) corresponding to three Reynolds numbers regions such as: low, intermediate, high. Rear stagnant cap model was used to estimate the required amount of surface active molecules that, cause retardation and full immobilization of bubble surface, which explains the reason of high sensitivity of small bubbles for even trace amount of surface active impurities.

The existing literature on the rise velocities of air bubbles in aqueous surfactant solutions adsorbing at the water-air interface focusses mainly on large bubbles ( $D > 1.2 \text{ mm}$ ). In our study smaller air bubbles ( $D < 505 \mu\text{m}$ ) were employed to investigate the effect of the bubble size on the detection of two flotation frothers of different adsorption kinetics via bubble rise velocity measurement. The influence of the bulk concentration of flotation frothers on the bubble rise velocity and the degree of tangential mobility was discussed. Additionally, the tangential mobility at the bubble surface was compared with the equilibrium interfacial tension and correlated with the surface coverage determined from the adsorption isotherms.

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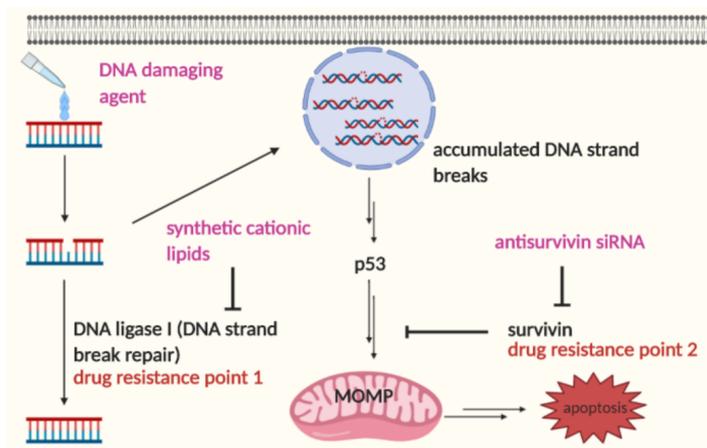
# Novel antitumor cationic cubosomes deployed for the combination therapy of drug-resistant cancers

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Lipid-based nanocarrier systems have gained enormous attention in the medical field due to their high biocompatibility and ability to improve the therapeutic efficacy of encapsulated drugs. However, the therapeutic efficacy of the latter is compromised in certain diseases (like cancer), due to highly complex pathways associated with the disease development, demanding multiple pharmacological interventions. Hence, herein we aim to address this challenge by co-delivering the traditional chemotherapeutic agent and survivin siRNA using cubosomes constituted of novel synthetic antitumor cationic lipids (anti hLigI inhibitors)<sup>1</sup> wherein the siRNA and cationic lipid act independently on different complimentary targets to sensitize the drug-resistant cancers to the chemotherapeutic agent (paclitaxel/doxorubicin) employed.



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# The importance of diffusiophoresis in promoting small-on-top stratification in drying films

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Stratification in drying films – how a mixture of differently-sized particles arranges itself upon drying – is examined. It is seen experimentally that smaller particles preferentially accumulate at the top surface, but it is not understood why.<sup>1</sup> Understanding this could allow the design of formulations that self-assemble during drying to give a desired structure. Potential applications are across a wide range of industries, from a self-layering paint for cars, to a biocidal coating in which the biocide stratifies to the top surface, where it is required.

On the basis of diffusional arguments alone, it would be expected that larger particles stratify to the top surface. However, other physical processes, including diffusiophoresis, may also be important. By deriving transport equations, the magnitude of different contributions can be compared, and numerical solutions for the film profile are produced.

This work probes the significance of diffusiophoresis: to the diffusional model, a diffusiophoresis term is added that can be varied in strength. For hard spheres, it is predicted that diffusiophoresis counteracts the effect of diffusion, resulting in approximately uniform films. When the diffusiophoresis strength is increased, the small particles are predicted to stratify to the top surface. This suggests that diffusiophoresis does contribute to experimental observations of small-on-top stratification, but it might not be the only promoting factor.

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# An Open Microfluidic Chip for Continuous Sampling of Solute from A Turbulent Particle Suspension

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High solids content complicates in situ analysis of chemical processing, biological suspensions, and environmental streams. In most cases, analytical methods require at least one pre-treatment step of a small volume of sample before a particle-free fluid can be analyzed. We have developed a continuous in situ sampler that can “sip” particle-free solution from a turbulent high solids content stream (a slurry).<sup>1</sup> An open microfluidic chip with an extended slit opening shields the internal laminar flow from the turbulence outside. Unlike other open chips, our chip does not require close proximity to a solid surface and operates in turbulent environments for hours without maintenance. Two applications are demonstrated: monitoring iron(III) in a stirred slurry of mixed ore particles at high solids loading (4%wt) and paracetamol tablet dissolution profiles for two different formulations.

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# Pure water-air interface is mobile and bounces bubbles stronger

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The question of water-air interface mobility has been long debated. Modelling of free-rising bubbles bouncing from water-air interfaces has concluded that the water-air interface is always immobile in practical situations due to trace amounts of contamination<sup>1</sup>. Recently we conducted experiments using extra pure perfluorocarbon liquid, which demonstrated that a free-rising bubble would bounce more strongly from mobile than an immobile liquid interface<sup>2</sup>. To examine this effect in the case of pure water, we compared the bounce of millimetre-sized free-rising bubbles from a pure water-air interface with the bounce from a water-air interface on which a Langmuir monolayer of arachidic acid was deposited<sup>3</sup>. The monolayer concentration is low enough not to change the surface tension but high enough to immobilize the interface due to Marangoni stress effects. Bubbles were found to bounce stronger (by a factor of up to 2.0, Fig. 1) from the pure water interface compared to the Langmuir monolayer deposited interface. These experiments demonstrate that a pure water-air interface behaves like a mobile liquid interface in our systems. Numerical simulations support these experimental findings.

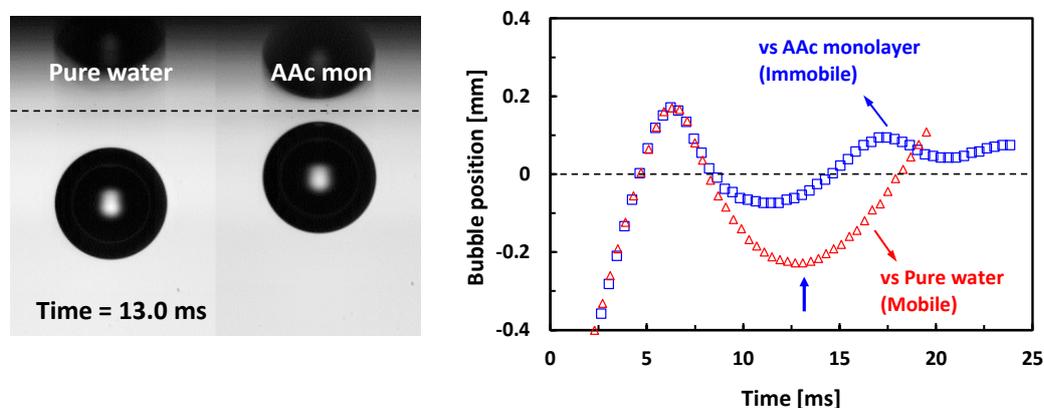


Fig. 1. Comparison of a 0.78 mm free-rising bubble bouncing from the pure water-air interface and arachidic acid (AAC) deposited on the water-air interface.

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## Microfluidic Screening to Study Acid Mine Drainage

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Acid mine drainage (AMD) is the most significant environmental pollution problem associated with the mining industry. Case-specific testing is widely applied and established in the mining and consulting businesses for AMD prediction, and any improvements in its efficiency, while reducing its environmental impact, are of utmost societal importance. Our group has successfully developed microfluidic platforms for screening mineral dissolution (leaching) chemistry.<sup>1,2</sup> In this study, we develop a microfluidic screening method as a useful tool in the prediction and, potentially, prevention and remediation of AMD.<sup>3</sup> The new approach offers key advantages including high throughput screening of reaction conditions, better spatiotemporal control over the process, and ability to conduct field-based measurements, which will account for specific interactions between mineral ores and their environment. Reagent and sample consumptions are greatly reduced to mL and mg levels, compared with those in conventional bulk-scale screening. Parallel (multichip) screening of ferric ion concentration gradients (0–40 mM) and temperature (23–75 °C) is demonstrated here, showing that the dissolution rate of pyrite significantly changes with the pH, temperature, and the ferric ion concentration, consistent with previous bulk-scale studies. To verify the robustness of the method, a mine waste rock was also tested in the microchip with natural waters. This study demonstrates the application of microfluidic screening to the challenging issue of AMD and, more generally, forecasting and optimization of mineral leaching in industry.

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# Extended electrostatic decay lengths at very high salt concentrations: Examples and Implications

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Many colloidal properties are strongly dependent on the range and strength of Coulomb interactions. In the presence of other ions, the Coulomb interactions between ions are screened such that the interaction energy between charges is exponentially dependent on the separation, this is often expressed in terms of the Debye length.

The surprising observation of long-range electrostatic forces between surfaces immersed in ionic liquids and concentrated salt solutions<sup>1-5</sup>, has recently shown that at high electrolyte concentrations the electrostatic decay length is clearly *not* described by the Debye length and that the electrostatic decay length shows a minimum beyond which the range of electrostatic interactions *increases* with increasing electrolyte concentration.

Several examples of systems that exhibit long-range interactions at high salt concentrations will be presented and the implications discussed.

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## **Adelaide – Poster Abstracts**

# Investigating the Structure of Tethered Bilayer Lipid Membrane (tBLM) in the Presence of Liquid by Ion Scattering Spectroscopy

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Tethered bilayer lipid membranes (tBLMs) are solid supported membranes, where the solid supported substrate is separated from the artificial lipid bilayer by an anchorlipid such as 2, 3-di-O-phytanyl-glycerol-1-tetraethylene glycol-D,L-lipoic acid ester lipid (DPhyTL). Tethered bilayer lipid membranes are based on self-assembled monolayers (SAMs) of anchorlipids. The chemical structure of the tether-segment of the anchorlipids has a significant effect on the properties of the artificial tethered bilayer lipid membranes such as its fluidity. Therefore, this study focuses on investigating the structure of tBLM based on DPhyTL anchorlipid in the presence of liquid e.g. formamide and water by ion scattering spectroscopy (ISS). Neutral impact collision ion scattering spectroscopy NICISS is one of the ion scattering techniques. It is a vacuum-based technique that employed for investigating the composition and structure of soft matter surfaces. NICISS measures the concentration depth profiles of elements present in the sample. Other surface analytical techniques will be applied such as X-ray photoelectron spectroscopy (XPS). XPS is applicable to determine the elemental composition and chemical state of elements present in the sample. Electrochemical impedance spectroscopy (EIS) is a commonly used technique to confirm the presence of lipid bilayers and the quality of it through the presence of electrochemical properties before applying NICISS and XPS techniques. The main purpose of understanding the structure of tBLM will help in further development and adjustment of the structure of the membrane to mimic a real membrane, thus, using them as sensor devices.

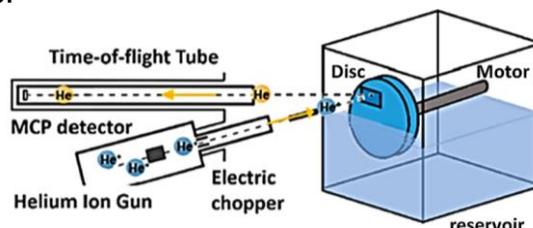


Figure 1: A schematic illustration of the design used for liquid sample target in NICISS. This figure is adapted from (1)

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# Interfacial Study of Aged Dye Sensitised Solar Cell to Investigate the Degradation Phenomena Introduced Under Different Stress Factors

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Dye Sensitised Solar Cells (DSSCs) are a strong candidate among the third-generation thin films solar cells with a simple and inexpensive manufacturing process, eco-friendly nature, and good cost-to-performance ratio which uses low-cost materials. The commercialization of DSSCs demands high efficiency with good stability and hence, the understanding of aging and instability is very crucial. Though aging studies is not a new topic to investigate, it still lacks an effective methodology to clarify the aging and instability caused by the degradation of individual cell component. This research focuses on setting up a procedure to understand ageing and the cause of instability in high performing DSSCs. To approach the aim, it is intended to reproduce efficient cells with easily and commercially available resources, considering the cost-effective property of DSSCs. Thus, reproduced cells are further exposed to different stress factors. The influence of the applied stress on the cell performance is tracked using Solar Simulator and further investigated using the surface analysis techniques, XPS (X-ray photoelectron spectroscopy), MIES (Metastable induced electron spectroscopy), UPS (Ultraviolet photoelectron spectroscopy), and FTIR (Fourier transform infrared) to understand the surface and interfacial change introduced due to ageing. NICISS (Neutral impact collision ion scattering spectroscopy) is involved to investigate the concentration depth profile for heavy elements like Ruthenium and Iodine the representative of dye and the electrolyte respectively. Additionally, the study aims to include ARXPS (Angle-resolved x-ray photoelectron spectroscopy) an effective depth-profiling technique complimenting FTIR spectroscopy for a better understanding of dye adsorption modes.

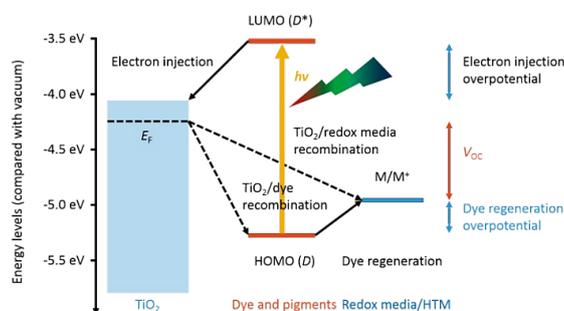


Fig: The schematic energy diagram and operating principle of a DSSC

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## **Brisbane**

8/2/21 – 9/2/21

## **Brisbane – Keynote Abstracts**

## Nano-Structured Dynamic Polymeric Particles Design by Light

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### Biography

Christopher Barner-Kowollik, Australian Research Council (ARC) Laureate Fellow, graduated in chemistry from Goettingen University, Germany, Christopher joined the University of New South Wales in early 2000 rising to lead the Centre for Advanced Macromolecular Design in 2006 as one of its directors. He returned to Germany to the Karlsruhe Institute of Technology (KIT) in 2008, where he established and led a Centre of Excellence in soft matter synthesis. He moved to QUT in early 2017 and established QUT's Soft Matter Materials Laboratory. Christopher's research achievements have been recognised by an array of national and international awards including the coveted Erwin Schrodinger Award of the German Helmholtz Association and most recently the United Kingdom Macro Medal. He is a Fellow of the Australian Academy of Science, the Royal Society of Chemistry and the Royal Australian Chemical Institute

### Abstract

The tuning of both covalent bond formation as well as dissociation remains a grand challenge in the design of photodynamic systems. The light-responsive adaptation of polymer materials requires different wavelengths to induce reversible covalent bond formation and dissociation. Our efforts have been devoted to pioneer a toolbox of photocycloadditions that can be triggered by lower energy visible light, while their cycloreversion should function at the least energetic wavelength, too.

The lecture will showcase a new method for the photoinitiated, additive-free precipitation-driven synthesis of particles by crosslinking pre-synthesized low molecular weight polymers. Microspheres were produced by employing the nitrile-imine mediated tetrazole-ene cycloaddition reaction upon UV irradiation ( $\lambda = 300$  nm), therefore forming intrinsically fluorescent particles.<sup>1</sup> The reaction wavelength was subsequently red-shifted to 415 nm by exploiting o-quinodimethanes that undergo [2+4] cycloadditions with suitable dienophiles or [4+4] via self-dimerization.<sup>2</sup> Critically, a variety of crosslinking molecules and dienophiles were investigated, imparting unique properties to the particles such as acid triggered fluorescence switch-on.<sup>3</sup> Finally, we explored the visible light-triggered reversible triazolinedione (TAD) chemistry as a dynamic covalent cross-linking platform that enables green light-induced particle formation (525 nm), while particle degradation is triggered by merely switching off the light. Herein, we combined our visible light driven particle design platform technology with the visible light-driven reversible [2+4] cycloaddition of triazolinedione (TAD) with naphthalene prepolymers, creating degradable microparticles that do not require any external degradation trigger other than darkness.<sup>4</sup>

## **Liquid marbles and liquid beads: handling tiny amounts of liquid like solid particles**

Nam-Trung Nguyen

### **Biography**

Nam-Trung Nguyen received his Dip-Ing, Dr Ing and Dr Ing Habil degrees from Chemnitz University of Technology, Germany, in 1993, 1997 and 2004, respectively. The habilitation degree (Dr Ing Habil ) is the qualification for a full professorship in Germany. In 1998, he was a postdoctoral research engineer in the Berkeley Sensor and Actuator Center (University of California at Berkeley, USA). Prof Nguyen is the First Runner Up of Inaugural ProSPER.Net-Scopus Young Scientist Awards in Sustainable Development in 2009 and the Runner Up of ASAIHL-Scopus Young Scientist Awards in 2008. He is a Fellow of ASME and a Member of IEEE. Nguyen's research is focused on microfluidics, nanofluidics, micro/nanomachining technologies, micro/nanoscale science, and instrumentation for biomedical applications. He published over 450 journal papers with over 23,000+ citations (Google Scholar) and filed 8 patents, of which 3 were granted. Among the books he has written, the first and second editions of the bestseller "Fundamentals and Applications of Microfluidics" were published in 2002 and 2006, respectively. His latest book "Nanofluidics" was published in 2009. The second edition of the bestselling book "Micromixer" was acquired and published by Elsevier in 2011.

### **Abstract**

Liquid marbles are droplets with volume typically on the order of microliters coated with hydrophobic powder. Liquid beads are core-shell beads with a liquid core and a solid shell. Both have sizes ranging from tens of micrometres to a few millimetres. The versatility, ease of use and low cost make both liquid marble and liquid bead attractive platform for digital microfluidics. These platforms allow for handling liquid with tools and methods used for solid particles. The talk will report our recent discoveries in the physics of liquid marbles and liquid beads that allow liquids to be manipulated as solids, as well as their robustness in terms of evaporation and structural deformation. The talk will also present applications such as large-scale three-dimensional cell culture, cryopreservation and polymerase chain reaction.

## **Molecule-by-molecule positioning at the solution/solid interface**

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### **Biography**

Jennifer MacLeod holds MSc and PhD degrees in Physics from Queen's University (Canada), where she worked on instrumentation development for scanning tunneling microscopy studies of semiconductor surfaces. She went on to hold an NSERC Postdoctoral Fellowship at the Università degli Studi di Trieste (Italy) and a Research Associate position at INRS (Canada). She joined QUT in 2015, where she has held an ARC DECRA Fellowship, and is currently Associate Professor and Head of School of Chemistry and Physics. Her research interests include self-assembly and reactions of molecules at surfaces, and the growth and modification of graphene and other 2D materials. She draws on a range of experimental and computational techniques, with a focus on using scanning probe microscopy and x-ray photoelectron spectroscopy (XPS) to elucidate these systems.

### **Abstract**

Achieving precise control of molecular self-assembly to form designed three-dimensional (3D) structures is a major goal in nanoscale science and technology. Using scanning tunnelling microscopy and density functional theory calculations, we have investigated the use of a single-atom-thick 2D covalent organic framework (COF-1) to template solution processed guest molecules.[1] This versatile approach can be used to trap and organize molecules at the solution/solid interface and in the subsequently obtained dried films. The molecular adsorption geometries depend on the solvent used for processing, and through the use of different solvents different (pseudo)polymorphs can be obtained. These template films can grow vertically, transition from two-dimensional to three-dimensional, which indicates that these nanoscale COF-1 templates may enable novel packing geometries suitable for device applications.[2] Furthermore, the relatively weak guidance provided by the templates allows flexibility in packing geometries, which can foster the formation of mesophases.[3] The approach can also be used to pattern molecules that have intrinsic barriers to forming periodic lattices, such as molecules with five-fold symmetry.[4] This suggests that monolayer templates may allow molecules designed specifically for function, rather than for crystallization into regular lattices, to be used in applications where crystallinity is desirable.

## **Bioinspired nanomaterials for drug delivery and biomimetic devices for drug screening**

Associate Professor Chun-Xia Zhao, Group Leader, UQ Amplify Fellow  
Australian Institute for Bioengineering and Nanotechnology; UQ, St Lucia, Australia.

### **Biography**



**Associate Professor Chun-Xia Zhao** is currently a Group Leader, UQ Amplify Fellow, UQ Node Leader and Program Leader of an ARC Centre of Excellence, at Australian Institute for Bioengineering and Nanotechnology, UQ. She was an ARC Future Fellow (2015-2019), and an Australian Postdoctoral Fellow (2011-2014). She leads a research team with a focus on the development of bioinspired micro/nanostructures for drug delivery and bioinspired devices (e.g. organs-on-a-chip models) for drug screening and evaluation. She has been focusing on innovative research as evidenced by her six patents, and one of her patented technology has been licensed to an international company. A/Prof Zhao's research has attracted more than \$7 M in research funding since 2011, including an ARC Centre of Excellence project (2020-2027), six Australian Research Council projects as the lead investigator, two national prestigious fellowship, many UQ grants and industry projects since 2011. She has been recognised for scientific excellence with a 2016 UQ Foundation Research Excellence Award. She has been appointed as member of the Australian Research Council College of Experts (2019-2021). She has published in top journals (Nature Comm, Science Advances, Angewandte Chemie, ACS Nano, etc.), and has delivered more than 20 keynote and plenary talks in international conferences. She serves as the Editor-in-Chief and Editors for several journals, and also reviews articles for top journals (Nature Comm, Angewante, Advanced Materials, Biomaterials, etc.).

### **Abstract**

Engineered nanomaterials have attracted enormous interest for drug delivery in the past decades. They hold great promise due to their unique properties such as nanoscale size, controlled drug release and their potential in targeted delivery. A wide range of nanomaterials have been developed for drug delivery, ranging from inorganic, organic, polymer particles to lipids, proteins and other synthetic compounds. However, their clinical translation has been limited. This demonstrates the huge gap between laboratory research and clinical translation of nanomedicines, mainly due to the incomplete understanding of the complex interactions between nanoparticles and the biological systems is lacking. My research team during the past years have developed novel approaches for producing bioinspired nanoparticle libraries with reproducible and systematically varied properties. Through systematic studies, a new physical attribute – nanoparticles' mechanical property – was discovered to play a crucial role in regulating their biological functions. Also, we developed patented technologies to increase the drug loading of nanoparticles from normally 1-5% to 65%, which presents huge advantages in improving treatment efficacy and in reducing undesirable effects from over-dosed nanomaterials. My group has also developed microchip-based models (Tumor Chips, Tumor-

Vasculature-on-a-Chip) for fast drug and nanomedicine screening. The development of our nanoparticle libraries and our biomimetic devices has improved the fundamental understanding of the complex bio-nano interactions, and provides new design rules for next generation nanomedicines.

## Rheology and Colloidal Properties of Nanocrystalline Cellulose Aqueous Suspensions

Yuan Xu (ACIS thesis prize)

### Abstract

Nanocrystalline cellulose (NCC) colloidal rods exhibit complex colloidal phase behaviours in aqueous suspension that are dependent on volume fraction and interparticle forces. The cholesteric liquid crystal phase and gel/soft-glassy phase are of significant interest because they have an ordered structure and allow solid-like response at relatively low solids fraction, respectively. The dimensions and morphology of NCC particles vary significantly with the type of raw material, which causes inconsistencies in behaviours reported between different works. This thus has led to empirical descriptions of structure-property relationships for individual NCC systems in the literature.

Rheology is used to map the phase properties and boundaries across a wide compositional range of NCC suspensions. A hypothesis is that the variation in NCC concentration and interparticle forces (manipulated by ionic strength) are sufficient to describe the complex phase behaviours anticipated within suspensions formulated using NCC obtained from different sources.

Here we reported the precise boundaries between, five phases that vary in their rheology and structure: viscous liquid, viscoelastic liquid, repulsive glass, attractive glass and gel. Based on this comprehensive phase map, we discovered a soft solid state with liquid crystal (LC) features which we termed liquid crystal hydroglass (LCH). The unique biphasic structure of LCH permits reversible orientation of the colloidal rods in LC phase i.e. alignment of NCC particles in LC phase is programmable. A key finding is the development of a generalised phase diagram for sulphonated NCC suspensions as function of ionic strength (interparticle forces), NCC dimension and concentration. By plotting in this manner (figure 1), the phase transition points for NCCs obtained from many sources and laboratories converge onto a single phase diagram. This work provides knowledge for formulating NCC-based materials with tailored rheology and microstructure, including control over structural anisotropy.

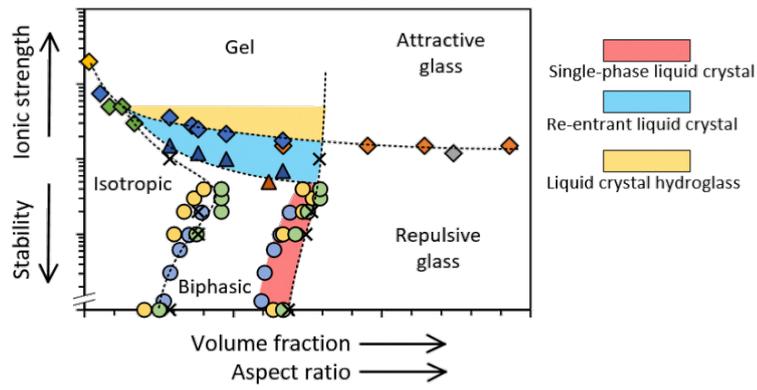


Figure 1. Generalised phase diagram of NCC aqueous suspensions. Markers represent phase transition reported in different literature [1].

## **Brisbane – Oral Presentation Abstracts**

# Dual-drug delivery of chemotherapeutic agents using targeted, pH-sensitive vesicles from self-assembled, degradable amphiphilic di-block polymers

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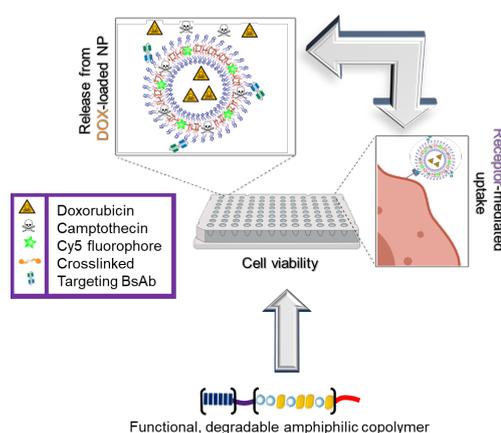
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Polymeric vesicles (i.e., polymersomes) have recently emerged as potential alternatives to traditional lipidic nanoparticles (e.g., liposomes). This comes due to their enhanced capabilities, appealing versatilities and competing therapeutic profiles. Polymersomes have also proved they are highly efficient in encapsulating and delivering a wide range of bioactive molecules, regardless of their hydrophilicities and affinities<sup>1</sup>.

This work describes the synthesis of functional macro-chain transfer agents<sup>2</sup> that were used to polymerise a combination of vinyl acetate (VAc), 2-methylene-1,3-dioxepane (MDO) and vinyl bromide (VBr) co-monomers, via reversible addition-fragmentation chain-transfer (RAFT) polymerisation. The produced functional, degradable amphiphilic di-block copolymers (Fig.1) were successfully utilized in forming stable, pH sensitive polymersomes. The formed vesicles were conjugated with targeting bi-specific antibodies (BsAb), then used to deliver the chemotherapeutic drugs Doxorubicin, Camptothecin, or a combination of both.

Vesicles morphologies, stabilities, drug encapsulation, release profiles and potential synergistic enhancement of cells killing, along with *in vitro* cytotoxicities and receptor-mediated drug uptake by MDA-MB-468 breast cancer cells were investigated and reported.

This work highlights the potential application of these nanoparticles in the area of drug delivery. The promising results we have obtained make us strongly believe that, with further *in vivo* and clinical investigation, these polymeric nanoparticles would show great potentials as next-generation cancer therapeutics.



**Figure 1** *In vitro* studies of self-assembled vesicles formed using di-blocks synthesized by RAFT polymerisation.

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# On differentiation of nanodroplets from nanobubbles: a study of molecular wetting of nanodroplets

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Nanobubbles are nanoscale gaseous pockets attached onto a surface immersed in water or freely suspended in bulk liquids. They have attracted great research interests in both fundamental sciences and industrial applications such as flotation and surface cleaning. The existence and stability of nanobubbles are longstanding controversial topics. Classical physical theory predicted that the spherical nanobubbles shall dissolve quickly into surrounding liquids, less than one second. The widely accepted theory intrigues the skepticisms over the existence and longevity of nanobubbles, which were reported ~ a few hours or days. The discrepancy spans a few orders of magnitude, which cast doubt that the observed objects are not nanobubbles, they are nanodroplets or nanoparticles instead. Moreover, researchers often suffer the difficulties in reproducibility of nucleation of nanobubbles and they suspected the observed objects are contaminations. A real challenge to overcome the skepticisms is to prove the nanobubbles are truly gaseous, *in situ*. Herein, we present a new way to distinguish nanodroplets from nanobubbles using atomic force microscope (AFM). Nanodroplets are found wetting into different geometric shapes and molecular films on graphite surfaces under water with different modified AFM tips. We discuss the possible mechanisms. This study contributes to a technology that differentiates nanodroplet from nanobubbles, and also get insight into better understanding of a nanodroplet on surface.

# Tribology of concentrated polymer brush grafted colloidal additives in rolling-sliding soft contacts

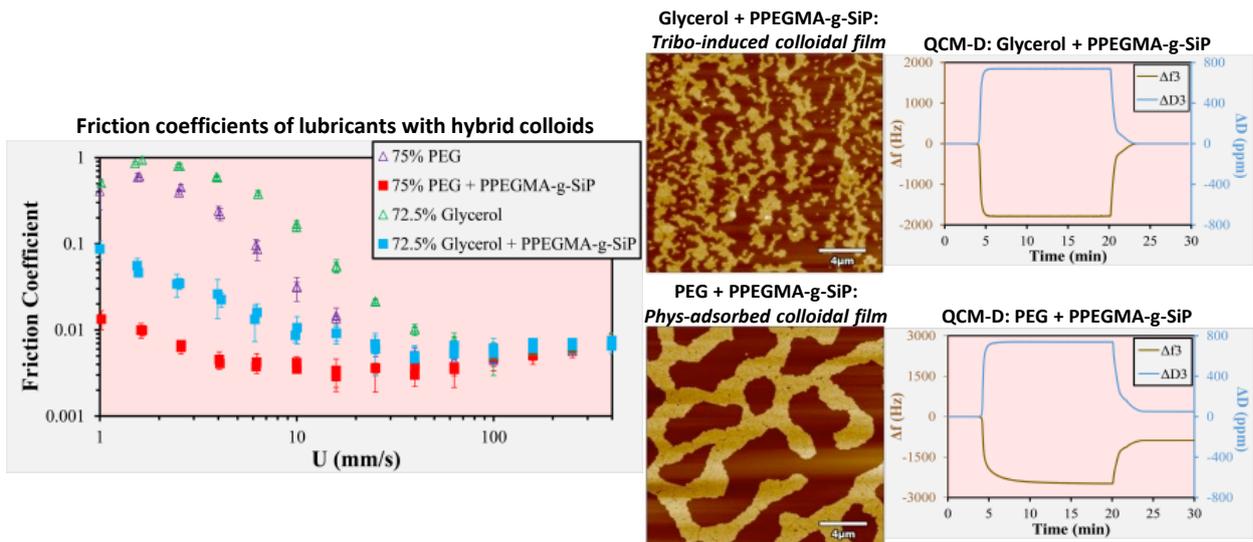
Amir Beheshti<sup>1</sup>, Yun Huang<sup>1</sup>, Idriss Blakey<sup>2</sup>, Jason R. Stokes<sup>1</sup>

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Tailoring surfaces by means of polymer brushes is a robust way to control friction and wear; however, wear of brushes hinders their real applications <sup>1</sup>. This study aims to introduce lubricant additives composed of concentrated polymer brush grafted colloids (hybrid colloids) for improved boundary and hydrodynamic lubrication. The incorporation of hybrid colloids in polyethylene glycol (PEG) significantly improved the lubricating properties at very low speeds by roughly two orders of magnitude. Hydrated colloids facilitated the hydrodynamic lubrication at lower speeds where they could maintain coefficient of friction at an ultra-low value (order of  $10^{-3}$ ). However, when they were tested in glycerol, they were deposited as a persistent film via the contact forces in the tribometer. The tribological performance (adsorption) of hybrid colloids in two solvents was also analysed using a quartz crystal microbalance (QCM). The two different observations mean that the film of hybrid colloids that form on the surface can be tuned and readily replenished from the lubricant, and provide a new strategy for obtaining super-lubricating surface coatings for both biotribological and engineering applications.



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# Spin Doctor – Synthesis of nitroxide coatings to prevent biofilm fouling

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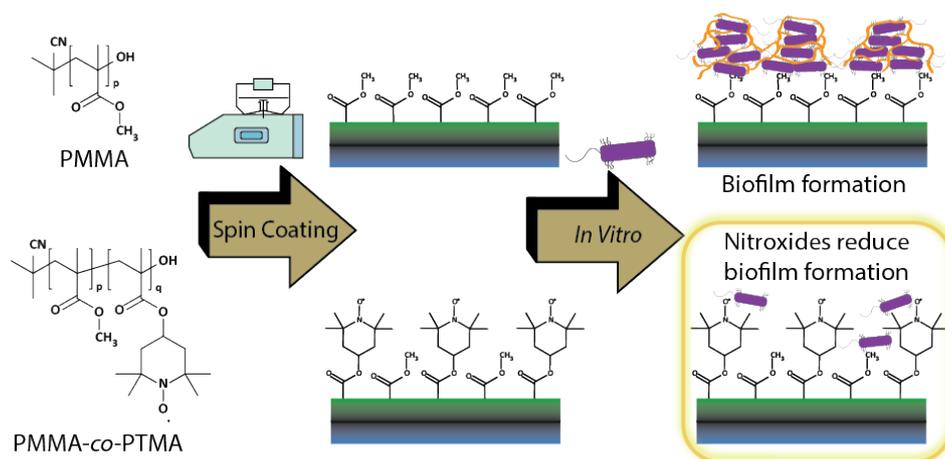
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Biofilms are highly organised colonies of bacteria and other microorganisms at a surface or interface. These colonies show a high level of structural complexity, which helps to protect the microorganisms from removal from a surface by both physical and chemical processes. Biofilms can cause major issues for industry and are also implicated in the vast majority of hospital acquired infections.<sup>1</sup>

Our research group has shown that small molecule nitroxides (persistent and stable free radical species) are able to inhibit the formation of biofilms on a surface, as well as being able to disperse existing biofilms.<sup>2</sup> In this project, we look to extend these molecules further by designing surface coatings and polymeric materials bearing pendant nitroxide groups<sup>3</sup>, which have the potential to be used as anti-biofilm surface coatings and nanoparticles. This talk will describe the different material classes that have been designed and synthesised, including functional silanes, copolymers, and photoactive materials. We will focus on investigating the dynamic behaviour of these materials on the surface using surface characterisation techniques including XPS, ellipsometry and QCM-D.



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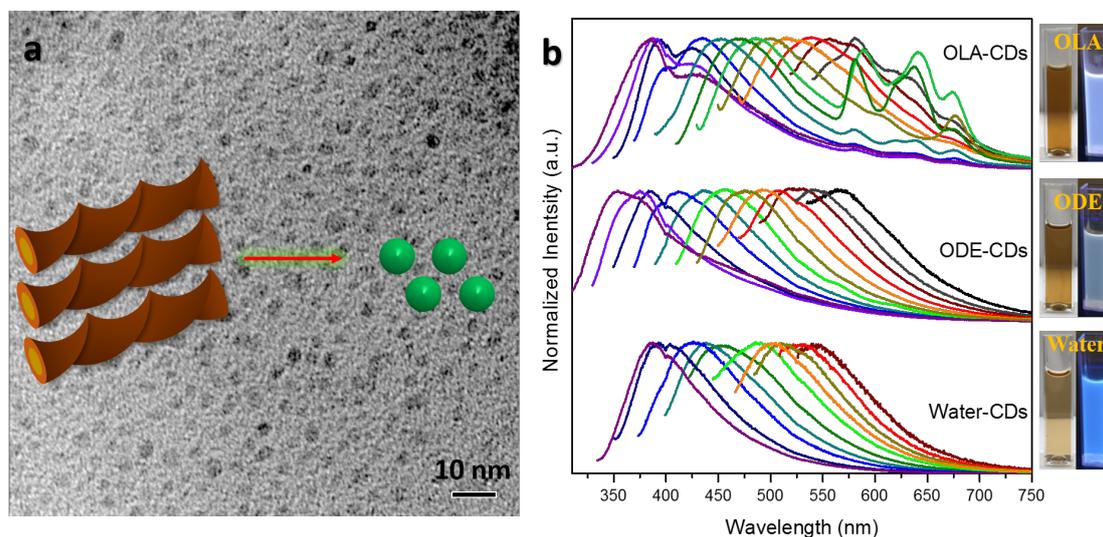
# Colloidal Synthesis of Seaweed-Derived Carbon Dots with Surface Passivation Induced Dual Emission

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Seaweeds are natural-abundant and environmentally friendly resources with hierarchical architecture and great biology compatibility. We present a general top-down and bottom-up method to attract high-quality carbon dots from biomass with surface ligand-induced dual emission through a colloidal synthesis strategy. The colloidal synthesis improved the quality of carbon dots in its size control and uniformity. The oleylamine-capped colloidal carbon dots showed the improved quantum yield and surface passivation induced dual emission, whereas having a strong selective emission response to the  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$ . The results revealed the surface function and interactions. Benefit from the good optical and colloidal stability, the seaweed-derived carbon dots demonstrated an excellent potential in selective monitoring of the dynamic variations of ions.



**Table of Content:** Seaweed-driven carbon dots and their emission.

# Topographical Discontinuous Dewetting for Patterning of Functional Material Colloidal Inks: Applications and Modelling of Process Parameters

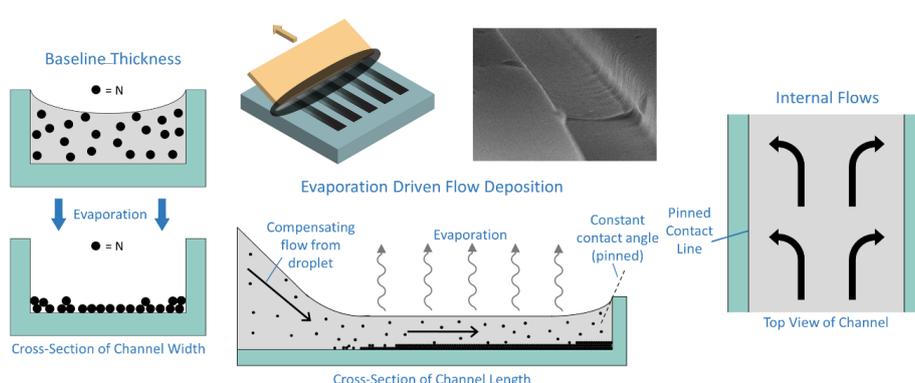
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Topographical discontinuous dewetting (TDD) patterning is a nascent 2D printing technique explored for high-throughput micro/nanoscale patterning of functional material inks. Using TDD we have patterned important functional materials at high-resolution, including conductive polymers like PEDOT:PSS and nanomaterials like carbon nanotubes,<sup>1</sup> with a view to use the technique for fabricating advanced devices.<sup>2</sup> TDD patterning involves selectively filling patterned, open cavities with functional material colloidal inks, depositing the functional materials into the open cavities in desired patterns. The deposited solidified materials in cavities can then be transferred to target substrates using liquid bridge transfer, allowing multiple patterned layers fabricated on the same substrate with potential roll-to-roll (R2R) compatibility.

However, variables affecting the z thickness and morphology of the deposited layers of functional materials inside the patterned microchannels are poorly understood. We developed a theoretical mathematical model that can determine the thickness of the deposited layers of functional material using the TDD patterning technique. Colloidal dispersions were deposited into microchannels using TDD patterning under various processing parameters to systematically study effects of different variables on the resulting deposited layer thickness/morphology.



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# Chemiluminescent Read-Out of Degradable Polymer Particles

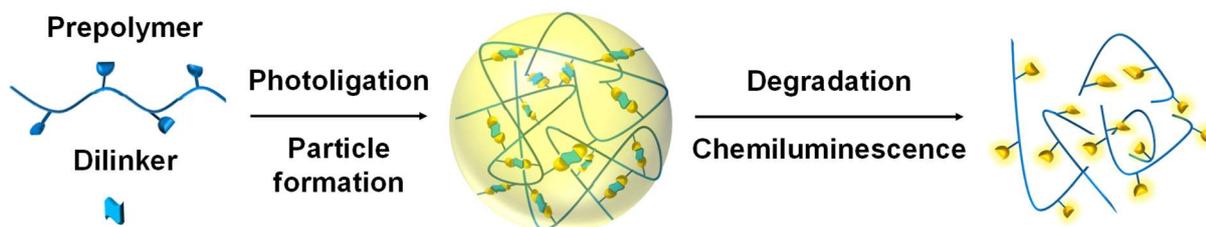
Laura Delafresnaye<sup>1</sup>, Jordan P. Hooker<sup>1</sup>, Christian W. Schmitt<sup>1</sup>, Leonie Barner<sup>1,2</sup>,  
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Polymer particles are an important and ubiquitous class of materials possessing an array of characteristics attracting wide-ranging application and continuous development. Underpinned by unreported photochemical reactions, we have recently developed a new platform technology for particle synthesis.

Specifically, we reported how well-defined polymers functionalised with photo-active moieties (tetrazole<sup>1</sup> or *o*-methylbenzaldehyde<sup>2,3</sup>) can be rapidly cross-linked into functional microspheres under UV or visible irradiation. Similar to a precipitation polymerization technique, the synthesis does not require any stabilizers, bases or initiators, and proceeds at ambient temperature to yield narrow dispersed microspheres in less than 2 hours. Moreover, control over the concentration, solvent combination and irradiation intensity led to a broad and tunable particle size range (0.2 – 5  $\mu\text{m}$ ). Importantly, the novel properties of the resulting moieties were translated to the particles (e.g. inherently or on-demand fluorescent particles) and these can be further functionalized through residual acrylate, alkyne and hydroxyl groups. As a prime example, fluorescent particles were formed by crosslinking a photoreactive polymer and a peroxyoxalate dilinker. The self-reporting microspheres can be degraded on-demand by addition of hydrogen peroxide that cleaves the linking points and subsequently disintegrates the particles. Degradation of the microspheres can be readily monitored by the light emitted via chemiluminescence.<sup>4</sup>



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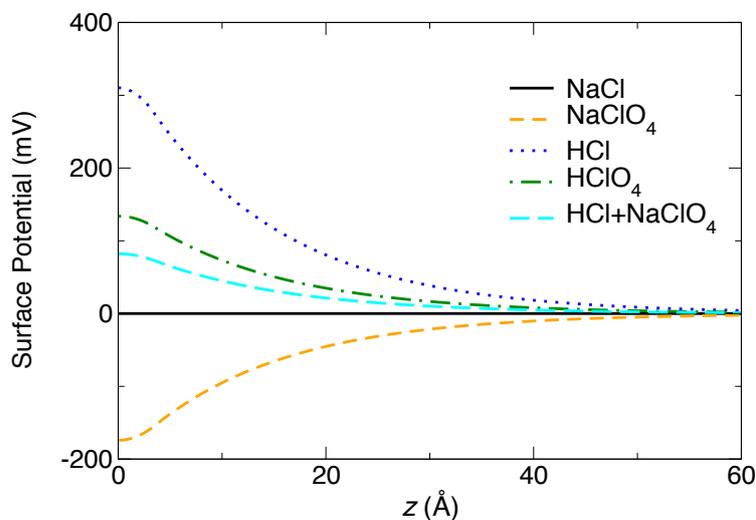
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## The surface potential is key to explaining ion specific bubble coalescence inhibition.

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Some salts have the peculiar ability to inhibit the coalescence of bubbles when added to solution. This is believed to be attributable to the enhancement or depletion of ions at the interface. However, this phenomenon is known to depend on which particular pairs of ions are present in a peculiar and unexplained way.<sup>1–3</sup> Here, a modified Poisson-Boltzmann model is used to demonstrate that these rules are attributable to the fact that certain combinations of ions create a substantial surface potential in order to satisfy the electro-neutrality condition. This surface potential acts to dampen the natural propensity of these ions for the interface in a way that explains the combining rules.<sup>4</sup>



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# Nanoscale Structure-Activity of Electrochemically Functional Metal Oxide Nanomaterials.

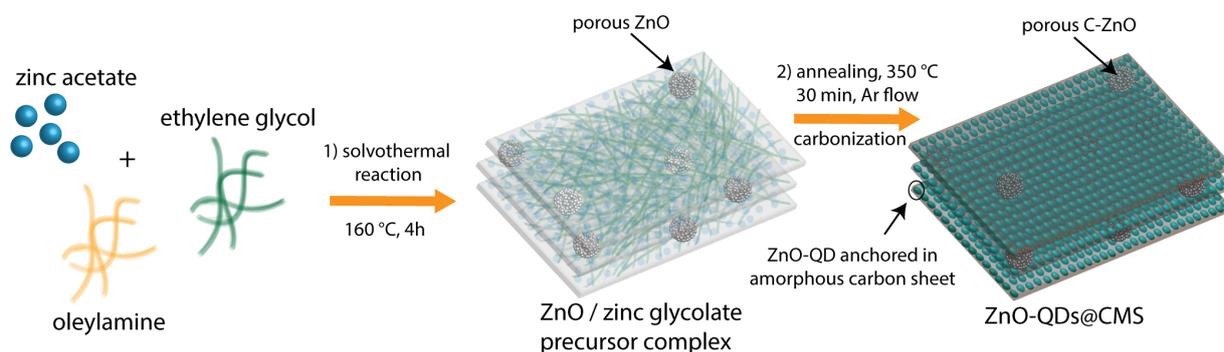
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The continuous growth of global population and the consequent demand for portable electronic devices, electric vehicles and renewable energy sources have urged the rapid advancement of secondary battery technologies. In this regard, electrodes based on metal oxides such as zinc, manganese and vanadium oxides are quite promising, owing to high reversible capacity, cycling stability and low cost. However, the practical applications of metal oxides are hindered due to the limited understanding of nanoscale structural activity that governs the energy storage capability of these materials. *In situ* transmission electron microscopy (TEM) has become a useful tool to systematically relate nanoscale phenomena at the electrode/electrolyte interface to the electrochemical signature in real time, and consequently generates new insights into the structure-activity of electrode materials. This presentation will focus on the recent findings based on *in situ* TEM, that would help the rational design of metal oxide/chalcogenide-based electrode materials for high performance rechargeable batteries. In one example, a simple and cost-efficient solvothermal synthetic route was developed to prepare a ZnO/carbon composite with excellent lithium storage properties (Figure 1). Using *in situ* TEM techniques, we discovered that amorphous carbon network not only effectively buffers the volume expansion of the composite electrode but also suppresses the growth of adversely large, stable Zn grains and eases the formation of a LiZn alloy during lithiation, which has a substantial contribution to the reversible capacity and stability displayed.



**Figure 1.** Schematic illustration of ZnO/carbon composite synthesis process. Reproduced from Ref. 1 with permission from The Royal Society of Chemistry.

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# Effect of NaCl on the air-liquid interfacial rheology in sodium dodecylbenzene sulfonate solutions

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Measurement of interfacial dilational rheology is a common technique to investigate interfacial viscoelastic properties of surface-active substances such as surfactants. Viscoelasticity of an interface characterises the response of the surface to shear and extensional stresses. Despite the maturity of studies of the surface rheology of mixed surfactant layers, only few investigations are available on the effect of salts on the interfacial rheology of surfactant solutions. Some of these studies report a decrease in the dilational viscoelasticity of the interface of surfactant solutions in the presence of inorganic salts such as NaCl (1, 2), while others conclude that inorganic salts increase the surface viscoelasticity of surfactant solutions (3, 4). This study examines the effect of NaCl on the adsorption of sodium dodecylbenzene sulfonate (SDBS) over a wide range of SDBS and NaCl concentrations.

Our results indicate that depending on the frequency of surface oscillation and surfactant bulk concentration, NaCl shows opposing effects on the dilational viscoelastic moduli of the gas-liquid interface. Our data also show a shift in the surfactant *transition concentration* (where the viscoelastic moduli reach their maximum values) towards smaller surfactant bulk concentrations with increasing salt concentration. It is attributed to suppressing the electrostatic repulsion between the hydrophilic head groups of surfactant molecules in the presence of NaCl.

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# Polysaccharides at fluid interfaces of food systems

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Fabrication of next generation polysaccharides with interfacial properties is driven by the need to create high performance surface active macromolecules that operate at extreme environments, as for example in complex food formulations or in the gastrointestinal tract. This contribution presents an overview of the behaviour of polysaccharides at fluid food interfaces focusing on pectic polysaccharides and their performance in the absence of any other intentionally added interfacially active components. The complex molecular structure of polysaccharides makes the assignment of structure vs. function relationships particularly challenging. Conformation of polysaccharides, as affected by the composition of the aqueous solvent needs to be closely controlled, as it seems to be the underlying fundamental cause of stabilisation events and appears to be more important than the constituent polysaccharide sugar-monomers. In addition, side chains, molecular mass, charge and charge density play important role in providing effective barriers to emulsion coarsening whereas protein content appears to have only ancillary role. Finally, polysaccharide adsorption is better understood by regarding them as copolymers, as this approach may assist to better control their properties with the aim to create the next generation biosurfactants. [1, 2]

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# Stable Polymer Nanoparticles with Exceptionally High Drug Loading by Sequential Nanoprecipitation

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Poor solubility often leads to low drug efficacy. Encapsulation of water-insoluble drugs in polymeric nanoparticles offers a solution. However, how to increase drug loading remains a critical challenge. Here, we report a simple and robust sequential nanoprecipitation technology to produce stable drug-core polymer-shell nanoparticles with high drug loading (up to 58.5%) from a wide range of polymers and drugs.<sup>1</sup> This platform technology used an organic solvent system containing two or more organic solvents to achieve the sequential precipitation of the drug and polymer. This method allows the precipitation of the drug preferably just prior to the precipitation of the polymer. We also showed the flexibility of this technology to encapsulate many hydrophobic drugs, such as paclitaxel, curcumin, ibuprofen, etc. Our *in vitro* and *in vivo* results confirmed the high-drug loading nanoparticles had enhanced therapeutic effect and improved safety. This technology offers a new strategy to manufacture polymeric nanoparticles with high drug loading having good long-term stability and programmed release and opens a unique opportunity for drug delivery applications.

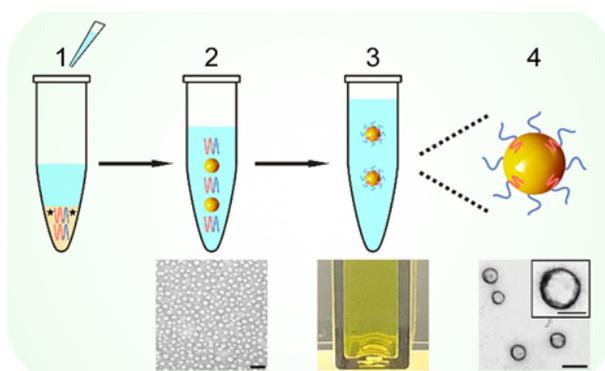


Figure 1. Schematic of sequential nanoprecipitation methods.

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## **Targeted delivery of novel immune-boosting peptides to both tumour and immune cells using polymeric nanoparticles to manage lung cancer**

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Lung cancer remains one of four leading causes of cancer death worldwide. Approximately 85% of lung cancers are non-small-cell lung cancers (NSCLCs). The average 5-year survival of NSCLCs is 15-20%. The dominant factors contributing to lack of curative therapeutic options for lung cancer are: 1) up to 70% of NSCLCs are diagnosed at the advanced stage with metastatic disease and are not suitable for curative treatment due to the low resection rates, 2) Heterogeneity and low antigenicity of NSCLCs result in low response rate to current targeted therapy and checkpoint inhibitors. Thus, novel therapeutic options for long-term treatment of NSCLCs are necessary for patients who have poor prognosis and therapeutic outcomes.

The development of immune boosting peptides has shown a great potential to boost exhausted T cells and works as a novel therapeutic agent against human lung cancer. Their translation for clinical use is limited by the ability to produce a site-specific response. Rapid growth in nanotechnology provides an opportunity to improve the pharmacokinetic and pharmacodynamic behaviour of drugs, suggesting that nanoparticles are the ideal platform for the targeted delivery of immune boosting peptide to the tumour site. We develop polymeric nanoparticles for the targeted delivery of immune-boosting peptides to both tumour and immune cells, and evaluate pharmacokinetics, biodistribution and tumour suppression properties of the immune boosting nanomedicine.

# Graphene and graphene heterostructures: 2D materials towards applications

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The rise of 2D materials, started with graphene, was followed by a surge of research into other layered crystals which consist of monolayers held together by van der Waals interactions. Surfaces and interfaces are very important to determine the properties of the final product. In this talk I will present our recent research around the development of some of these materials which are promising for applications.

By using exfoliated graphene and reduced graphene oxide we produce highly efficient all-carbon solid-state supercapacitors achieving capacitance of more than 400 F/g, with a technology that can be easily scaled up for industrial production<sup>1</sup>.

Lateral graphene - hexagonal Boron Nitride heterostructures for electronic applications have been obtained by a transfer free synthesis method, on epitaxial graphene grown on SiC, via Chemical Vapour Deposition. XPS, Raman and atomic resolution images provide an insight on the reaction mechanism that produces a chemical conversion of the epitaxial graphene into h-BN<sup>2</sup>. We show also the successful synthesis of WS<sub>2</sub>/graphene/SiC van der Waals vertical heterostructures which displays interesting properties for electronic applications. Finally, a study of the epitaxial growth of MoS<sub>2</sub>/graphene heterostructures on two completely different graphene substrates sheds some light on the growth mechanism of 2D heterostructures on graphene.

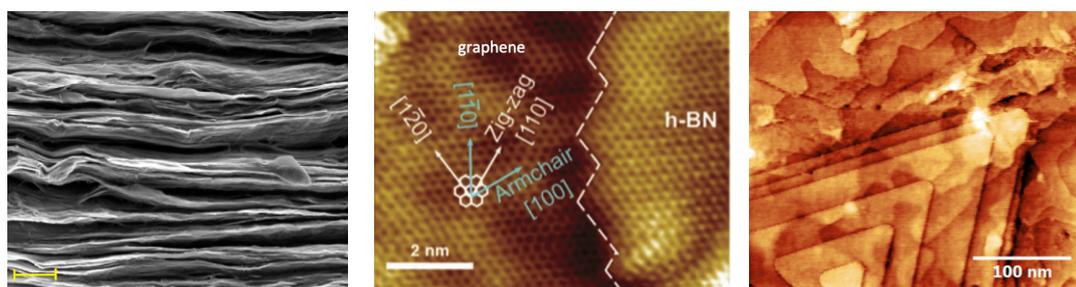


Fig1. Left: SEM image of a layered structure rGO film. Scale bar 500 nm. Centre: Atomically resolved image of h-BN/graphene interface obtained by Scanning Tunnelling Microscopy. Right: STM image of an island of MoS<sub>2</sub>/graphene/SiC

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## Modification of chitosan for cancer drug delivery applications

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Chitosan-based materials have a long history as drug delivery vehicles due to their characteristics of biodegradability, high drug carrying capability, and multifunctionality<sup>1</sup>. We are working on modification of chitosan with PEG and alendronate-PEG (Ald-PEG) to make curcumin (Cur), siRNA and Cur/siRNA encapsulated particles. Low molecular weight medical grade chitosan (Chi) was modified using PEG and Ald-PEG at different molar ratio of PEG and Chi by EDC/NHS coupling. <sup>1</sup>H NMR verified coupling of mPEG-COOH and Ald-PEG-COOH to Chi with a DS of 5-15 % and 8-15 %, respectively. Stability of Ald-PEG-COOH was evaluated by 2D DOSY for one week at 37 °C and found to be stable based on no free Ald detected. The solubility of Chi, mPEG-Chi and Ald-PEG-Chi was evaluated at a range of pH (4-8) and it was found that modified chitosan polymers had high solubility especially above pH 6 compared to chitosan. Nanoparticles were prepared by an ionic gelation method<sup>2</sup>. The particle diameter and charge were measured by dynamic light scattering (DLS) and further confirmed by transmission electron microscopy (TEM). The size of the particles was controlled < 100 nm and the zeta potential was in the near neutral range (-10 to 10 mV). Nanoparticle stability in terms of size and zeta potential was evaluated in 50 % serum and it was found that modified chitosan particles are more stable both in terms of size and zeta potential as compared to chitosan particles.

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## Design of surface-functionalised polycaprolactone: considering degradation and fate of modified biomaterials

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Polyesters including poly( $\epsilon$ -caprolactone) (PCL) are commonly used as biomaterial implants in bone tissue engineering. PCL is biodegradable, however it is hydrophobic and lacks functionality required for interaction with biological material (e.g. proteins). PCL can be surface-modified to introduce desired functionality and allow for protein binding and delivery.

Many recent studies on surface-modified polyesters have not investigated the effect of surface modification on the degradation of the substrate, or the fate of the surface layer itself.<sup>1</sup> Particularly when attaching a hydrophilic surface layer to a hydrophobic substrate it is important to assess if this modification will alter the degradation rate of the material's surface.<sup>2</sup>

In the present study PCL has been modified by gamma irradiation-induced grafting using two different monomers to introduce two different types of functionality. 2-Aminoethyl methacrylate (AEMA) has been used to introduce amines for conjugation to biopolymers that have good binding affinity for bone growth proteins, and 3-sulfopropyl acrylate (SPA) is used to introduce sulfonates for direct protein binding.

The surface layer stability was evaluated for modified PCL samples and it was found that the two relatively similar surface modification approaches resulted in vastly different stabilities of the graft copolymer in buffer solution.<sup>2</sup> Optimisation of the grafting process is required as the graft copolymers are not biodegradable. Parameters including monomer concentration and radiation dose were varied in order to yield graft copolymers that are small enough to be cleared from the body.

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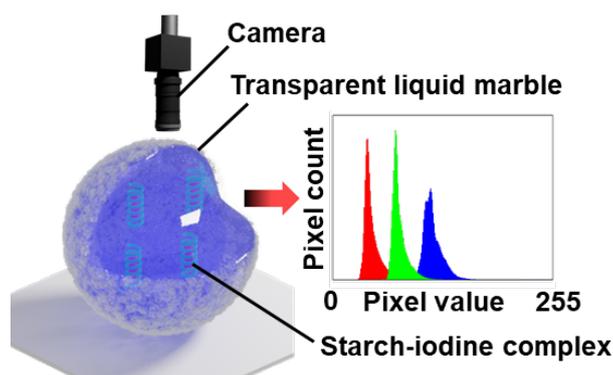
# Monitoring reaction in liquid marble miniaturised reactor using digital imaging-based colourimetry

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Miniaturised reaction systems have experienced soaring development in recent years. However, many microreactors platforms including continuous-flowing microfluidic reactors or droplet-based microreactors face difficulties such as rapid evaporation and difficult handling that limit their use in practical applications. In that context, miniaturised reactors based on liquid marbles, which are droplets stabilised by hydrophobic particles have emerged as promising candidates to overcome the weakness of other microfluidic reactor platforms. The coating particles completely isolate the interior liquids of liquid marbles from the surrounding environment, thus conveniently encapsulating the reactions. Liquid marbles can be manipulated like a soft solid, enhancing the potential of liquid marbles as microreactors<sup>1</sup>. Great efforts have been made over the past decade to demonstrate the feasibility of liquid marble-based microreactors for chemical and biological applications<sup>2</sup>. However, the use of destructive and ex-situ methods to monitor reactions impairs the potential of this platform. This study proposes a non-destructive, in situ, and cost-effective digital-imaging-based colourimetric monitoring method for transparent liquid marbles, using the enzymatic hydrolysis of starch as an illustrative example<sup>3</sup>. This monitoring method provides a facile, cost-effective and rapid means to investigate the reaction kinetics in liquid marble-based platforms.



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# Measuring the Effective Surface Tension of a Floating Liquid Marble Using X-ray Imaging

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A liquid marble (LM) is a droplet coated with microparticles that isolate the liquid interior from its surroundings, making it perfectly non-wetting. This attractive feature allows the LM to perform useful tasks such as coalescence,<sup>1</sup> targeted delivery, and controlled release. The non-wetting characteristics also allows the LM to float on a carrier liquid. The growing number of applications in digital microfluidics requires further insights into fundamental properties of a LM such as its effective surface tension. Although the coating provides the LM with various desirable characteristics, its random construction presents a major obstacle to accurate optical analysis. This paper presents a novel method to measure the effective surface tension of a floating LM using X-ray imaging<sup>2</sup> and curve fitting procedures<sup>3</sup>. X-ray imaging reveals the true LM liquid-air interface hidden by the coating particles. Analysis of this interface showed that the effective surface tension of a LM is not significantly different from that of its liquid content. We also found that our method is sensitive enough to detect small variations across individual LMs.

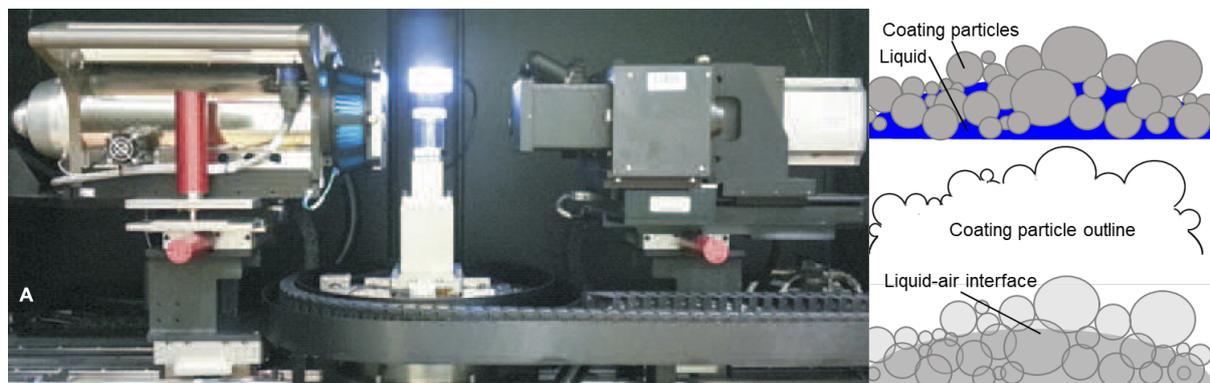


Figure shows the experimental setup of the imaging process and the schematic of the coating layer of a liquid marble.

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# Dewetting of poly(lactic-co-glycolic acid) and the implications when using thin films to model particle surfaces

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Poly (lactic-co-glycolic acid) (PLGA) is a polymer commonly used in nanoparticle delivery systems due to its biodegradability through hydrolysis of the polyester functionality and post-modification potential. Characterisation methods to analyse the chemical and morphological features of the particles can be limited in scope and simplicity compared to thin film surfaces. As a result, it is often more convenient to model the surface modification of particles with thin film studies. Significant work has used polyester thin films to investigate surface modification and adsorption of *in vitro* proteins for application in analogous drug delivery systems<sup>1-4</sup>.

Typical protocols for fabrication of thin films involves spin coating or dip coating of polymeric solutions onto pre-functionalised surfaces such as salinized silicon wafers or glass slides. When studied or modified in aqueous systems, amorphous polyesters of low T<sub>g</sub> (<50 °C) are known to swell and hydrolyse, resulting in localised hydrophilic domains causing deformation to ease thermodynamic, mechanical and osmotic stress. Consequently, the hydrophilic polymeric material can retract from the hydrophobic surface it was forced to cover; a process known as dewetting. Dewetting is unique to thin film studies on hydrophobic surfaces causing thin films to behave in a manner inconsistent with the particle surfaces.

This work utilises current advanced characterisation techniques to highlight the disjoint in using thin films to model particle surfaces, primarily caused by the dewetting process. Characterisation of PLGA thin films with ellipsometry, atomic force microscopy and X-ray photoelectron spectroscopy are judiciously compared with particles analysed by dynamic light scattering.

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# Enabling Diamond Nanoelectronics by Solid-State Surface Transfer Doping

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Despite being a bona-fide bulk insulator, diamond develops an intriguing two-dimensional (2D)  $p$ -type surface conductivity when its surface is terminated by hydrogen and exposed to appropriate surface adsorbate layer such as atmospheric water as a result of the surface transfer doping process. Consequently, the surface of diamond presents a versatile platform for exploiting some of the extraordinary physical and chemical properties of diamond, leading to applications such as chemical/biological sensing and the development of high-power and high-frequency field effect transistors (FETs).<sup>1</sup>

In this talk, I will begin with a review on the surface transfer doping of diamond by solid-state acceptors. I will describe our recent work on the surface transfer doping of diamond by transition metal oxides (TMOs).<sup>2</sup> Specifically, I will show that by interfacing diamond with  $\text{MoO}_3$  or  $\text{V}_2\text{O}_5$  a 2D hole conducting layer with metallic transport behaviours arises on diamond.<sup>3</sup> Magnetotransport studies at low temperature reveal phase coherent transport in the 2D channel with a transition from weak localisation to weak antilocalisation as temperature drops, and are analysed in the context of spin-orbit coupling induced by Rashba effect.<sup>4</sup> The obtained spin-orbit interaction is a few folds higher than that in the air-doped channel or ionic liquid gated channel with similar hole densities, suggesting that the local carrier density could in fact be much higher than that obtained by Hall-effect measurements. We also demonstrate that this surface conducting channel can be exploited to build diamond surface electronic devices such as metal-oxide semiconductor FETs (MOSFETs) which in turn allows us to tune the spin-orbit coupling strength in the 2D conducting channel using electrostatic gating.<sup>5</sup> Lastly, the prospects for constructing novel quantum devices on diamond surface by making use of this highly tunable 2D conducting layer on diamond are also explored.

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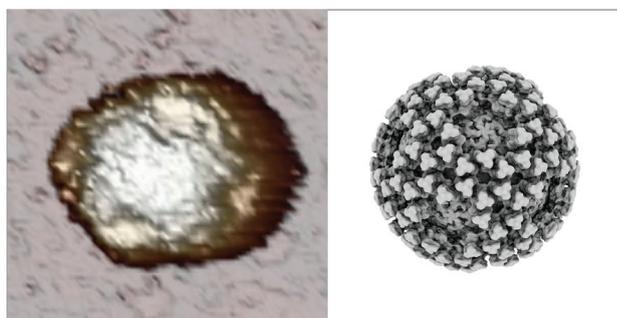
## Double-layer virus-like particles as robust biocatalytic nanoreactors

Lygie Esquirol<sup>1</sup>, Alvaro Ortega-Esteban<sup>2</sup>, Lou Brillault<sup>3</sup>, Michael Landsberg<sup>4</sup>, Pedro de Pablo<sup>2</sup>, Frank Sainsbury<sup>1</sup>

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Protein cages can act as a colloidal scaffold for encapsulated enzymes, increasing their stability whilst also allowing for the co-localisation of multiple enzymes in a pathway. In this way, they are advancing knowledge in enzyme behaviour and also hold considerable promise in applied biocatalysis. However, they have not yet lived up to their promise in industrial settings and understanding how protein cage architecture dictates their physical properties is central to their continued development. Here we investigate the physical properties of single- and double-layer particles assembled from Bluetongue virus coat proteins engineered to contain cargo proteins.<sup>1</sup> Using a combination of cryo-electron microscopy and atomic force microscopy, we find that the two particles have markedly different physical properties and that encapsulated cargo proteins influence the properties of both. The addition of the second protein layer provides a mechanical strength to the particles that also doubles the thermal stability with respect to the single-layer particles. The presence of cargo proteins imparts an increase in thermal stability on the single-layer particles, whereas no increase is found above the intrinsic stability of double-layer particles. Analysis of force indentation curves suggests that cargo proteins, shown to associate with the inner surface of the protein cage, provide a structural reinforcement to the single-layer particle that helps maintain interactions with the second, stabilising shell of the double-layer particle. Only the latter are functional as a biocatalytic nanoreactors in simulated industrial process conditions. These results advance fundamental understanding of protein cage design and use in biocatalysis.



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## **Lubrication of pH responsive polyelectrolytes as a function of macromolecular composition and sequencing**

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A combined experimental and theoretical approach is used to elucidate the molecular mechanisms governing the pH responsive lubrication behaviour of weak polyelectrolyte systems, using a series of pectin fine structure variants. The friction coefficient, measured using a soft contact ball-on-disc tribometer, is shown to depend on the density and distribution of ionisable groups, where macromolecular hydrogen bonding and hydrophobic polymer-surface interactions dictate the response at low ionisation (pH 2.5) and intra- and inter-chain electrostatic repulsion dominates at full ionisation (pH 6.5). Non-monotonic friction behaviour, observed during the transition from low to high pH, is shown to correlate strongly with the calculated electrostatic persistence length, highlighting the key role of electrostatic interactions and charge shielding effects driven by dissociated and external counterions. Normalised friction profiles, analysed in conjunction with two simple molecular models for non-ideal polyacid ionisation, provide compelling evidence to suggest that the pH responsive tribological behaviour of pectin, and potentially other weak polyelectrolyte systems, is directly dependent on the degree of ionisation adjusted for electrostatic and hydrogen bonding interactions.

# Designer Nanoparticles for effective cancer type specific immunotherapy

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Dynamic heterogeneity in cancer is the major challenge in the realization of successful long-term tumor eradication. In recent years, personalized cancer vaccines gained huge interest as a mean for tackling the above-mentioned challenge. Antigen-based cancer vaccines for personalized cancer immunotherapy relies on the identification of neo-antigens from an individual patient, which makes the vaccine manufacturing process more complicated, time-consuming and expensive. Tumor antigens (TA) are of great interest as these are over expressed in cancer cells and are potential in eliciting immune response against cancer. Nanomaterials have been employed for *in situ* capture and delivery of TA, however, limited efficiency in TA enrichment was observed due to the non-specific interaction between nanoparticle surface and TA. It is reported that certain types of cancer can go through certain types of post translational modification (PTM) aberrantly and TA also go through PTM during oncogenesis and progressions. Especially, breast cancer is reported to have elevated level of phosphorylation and this contributes to malignant phenotypes and tumorigenesis. Hence, we have designed a nanoparticle system surface modified with titanium for specific *in situ* enrichment of phosphorylated TA overexpressed in breast cancer. The PTM information extracted from proteomic studies are utilized in the design of nanoparticles tailored for effective enrichment of TA and its delivery. Customized nanoparticles showed extraordinary enrichment of phosphorylated TA and resulted in excellent efficacy in tumor inhibition *in-vivo*. The extent of cytotoxic T lymphocytes infiltration in distant tumor site was also enhanced for the animal group treated with the custom-made nanoparticles. It is expected that this new technology will pave the way towards convenient and affordable cancer immunotherapy with improved efficacy.

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# FUNCTIONAL NANOPARTICLES WITH GLUTATHIONE DEPLETION CHEMISTRY UPREGULATE MRNA TRANSLATION IN HARD-TO-TRANSFECT CELLS

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mRNA technology has been one promising hot topic particularly in light of the recent clinical trials of mRNA vaccines against COVID-19 pandemic and cancer immunotherapy. For successful mRNA vaccine, mRNA molecules are desired to be delivered to antigen presenting cells (APCs) for following protein expression. However, the hard-to-transfect nature in APCs has been a long-standing challenge. Nanomaterials have been applied for mRNA delivery, but the function is limited to delivery vehicles. Inspired by glutathione (GSH) related translation pathway and cell type dependent difference in GSH level, the impact of nanochemistry on mRNA translation modulation in hard-to transfect APCs has been firstly explored (Fig 1), exhibiting excellent mRNA delivery efficiency in APCs *in vitro* and *in vivo* compared to commercial reagents.<sup>1</sup> Furthermore, to overcome the GSH regeneration catalysed by glutathione reductase (GR), zeolitic imidazolate framework-8 (ZIF-8) mediated GR inhibition was firstly applied for long-term GSH depletion (Fig 2).<sup>2</sup> And imidazole group of ZIF-8 promoted endosomal escape could address the cytotoxicity from conventional polyethylenimine (PEI) modification in gene delivery. My finding has revealed the role of modulating mRNA translation, thus presenting a conceptual advance in the design principle of next-generation of mRNA delivery agents.<sup>3</sup> The imidazole group of ZIF-8 promoted endosomal escape and thus reduced the cytotoxicity derived from conventional polyethylenimine (PEI) modification in gene delivery. My findings have revealed the important role of modulating mRNA translation in gene delivery, presenting a conceptual advance in the designable synthesis of next-generation of mRNA delivery agents.<sup>3</sup>

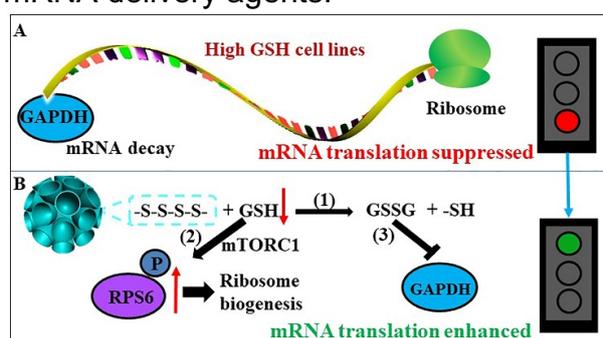


Fig 1

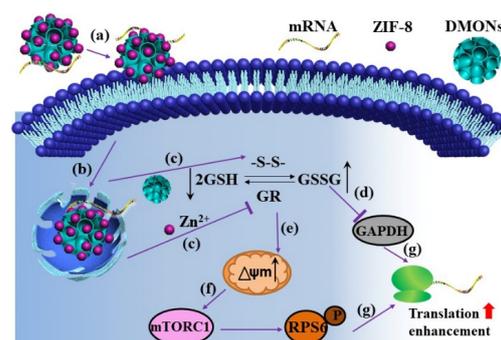


Fig 2

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# Synthesis of Lead Halides Perovskite Nanocrystals for Photoemission Applications

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In the past decades, perovskite compounds that use lead halides as framework in the crystal structure have received significant attention due to their success in solar cells. Currently the world-record efficiency of perovskite solar cells (>25%) is already comparable to the state-of-the-art crystalline silicon solar cells. The high efficiency PSC was achieved with cost-effective solution processing. Compared to the massive efforts to enhance performance of perovskite in solar cells and other applications, the mechanism for solution processing synthesis of perovskite materials in the form of both thin films and nanocrystals is much less studied. It is reported that the precursor that contains solid lead halides ( $\text{PbX}_2$ ,  $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) and organic (MAX, FAX) or inorganic halide ( $\text{CsX}$ ) is actually a colloidal that contains  $\text{PbX}_n$  species.<sup>1</sup> The properties of the colloidal depends on the solvent system used to form the perovskite precursor. In this talk, I will present our recent study of synthesis of lead halide perovskite nanocrystals by using ionic liquid based solvent medium<sup>2</sup>. I will show how the anions of ionic liquid salt influence the shape, dispersion and surface ligands of the perovskite nanocrystals. Consequently, this influence the photoemission property of the perovskite nanocrystals

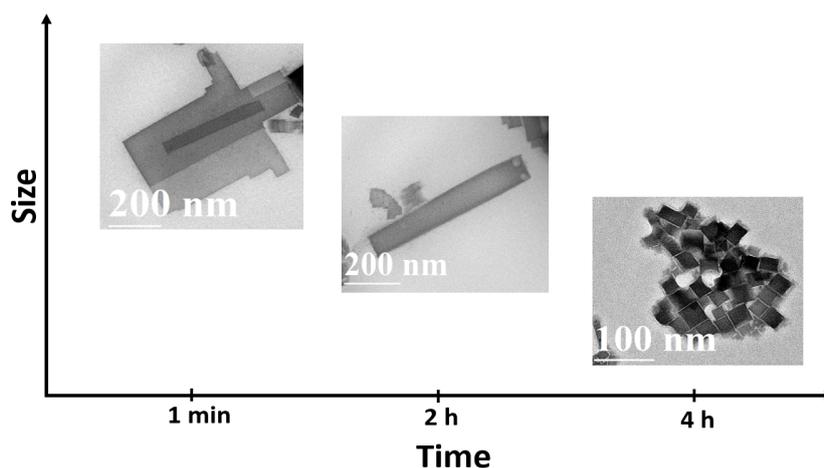


Figure 1. morphology evolution of perovskite nanocrystals as a function a reaction time.

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# Inorganic microcapsules for protection and efficient delivery of small molecule cargo.

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Control of the diffusion of small active ingredients is important for a wide range of applications that require delivery of ingredients in a specific place and timeframe. Encapsulation of the active ingredient in a protective shell is a common and useful technique to allow controlled release. Our group has developed novel encapsulation technologies to provide a complete barrier to the diffusion of small molecules until release is deliberately triggered. <sup>1-2</sup>

We recently discovered that deposition of a secondary shell of calcium phosphate onto a polymer microcapsule substrate allows for the complete retention of small molecule active ingredients and allows for improved control over release. The biocompatible nature of this mineral shell lends itself to a wide range of applications. The work presented here explores the controlled deposition of inorganic shells and subsequent release of the protected cargo, to address the inconsistencies associated with oral delivery of cannabinoid medicines.

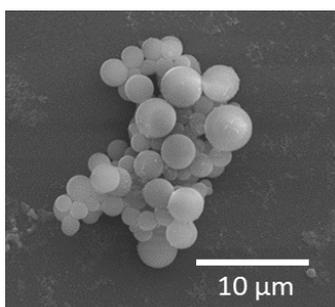


Figure 1 - Scanning electron micrograph showing calcium phosphate coated microcapsules

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## Metal oxide-chitosan compounds as theranostic modular nano-cocktails for ROS and inflammatory related diseases

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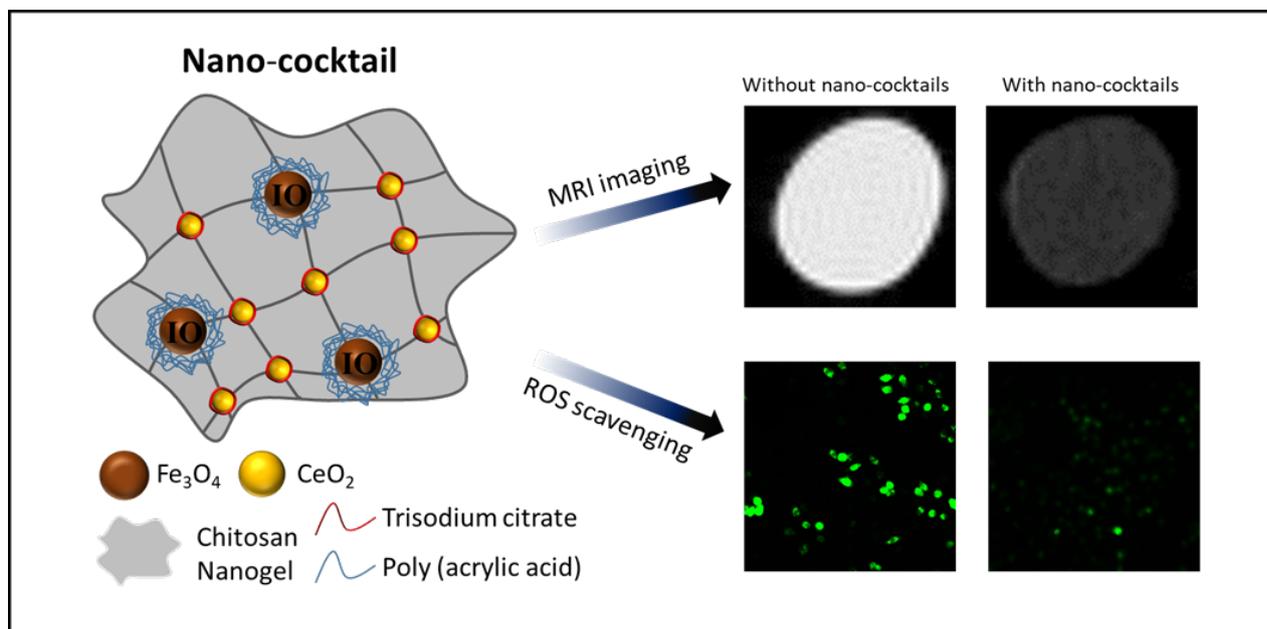
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Reactive oxygen species (ROS) play an essential role in the progression of many chronic diseases like atherosclerosis and rheumatoid arthritis. For decades, antioxidant compounds have always been considered as potential treatments for these ROS-related diseases. Concomitantly, non-invasive imaging systems such as magnetic resonance imaging (MRI) have also become widely used in the diagnosis of diseases, especially atherosclerosis. In this study, nanoceria utilised as therapeutic modules capable of ROS scavenging and iron oxide nanoparticles as imaging agents for MRI have been synthesised separately. Subsequently, two versions of theranostic chitosan nano-cocktails containing both nanoceria and superparamagnetic iron oxide nanoparticles (Chit-IOCO and Chit-TPP-IOCO) were successfully synthesised and methodically characterised. *In vitro* studies such as cytotoxicity, MRI and ROS scavenging were performed. The results indicate that Chit-IOCO nano-cocktails demonstrate outstanding potential for treatment and diagnosis of ROS-related diseases. Potentially, these nano-cocktails can be modified to include new modules, allowing more functions and applications.



# Bioinspired Core–Shell Nanoparticles for Hydrophobic Drug Delivery

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A large range of nanoparticles (NPs) have been developed to encapsulate hydrophobic drugs. However, drug loading is usually less than 10% or even 1%. Herein, core-shell NPs are fabricated having exceptionally high drug loading up to 65% (drug weight/the total weight of drug-loaded NPs) and high encapsulation efficiencies (>99 %) based on modular biomolecule templating. Bifunctional amphiphilic peptides are designed to not only stabilize hydrophobic drug NPs but also induce biomimetic silica formation at the nanodrug particle surface thus forming drug-core silica-shell nanocomposites. This platform technology is highly versatile for encapsulating various hydrophobic cargos. Furthermore, the high drug-loading NPs lead to better *in vitro* cytotoxic effects and *in vivo* suppression of tumor growth, highlighting the significance of using high drug-loading NPs.

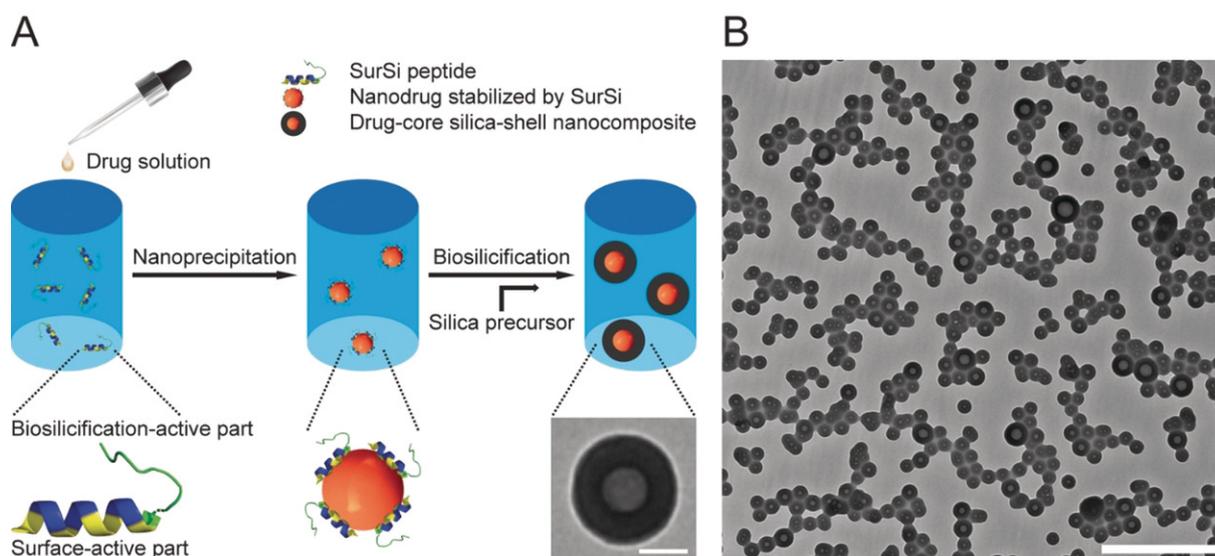


Figure 1. Design of drug-core silica-shell nanocomposites using a bifunctional peptide. A) Illustration of the synthesis process of drug-core silica-shell nanocomposites. Scale bar: 50 nm. Drug NPs were formed through nanoprecipitation and stabilized by a bi-functional peptide which could later induce the formation of a silica shell around the drug NP, creating the drug-core silica-shell nanocomposite. B) Representative transmission electron microscopy (TEM) image of curcumin-core silica-shell nanocomposites. Scale bar: 1  $\mu\text{m}$ .

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# Effect of various surface conditions on Van der Waals epitaxy of MoS<sub>2</sub>

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Combination of 2D layers of graphene and semiconducting TMDs (such as MoS<sub>2</sub>) as a synthetic Van der Waals heterostructure, have previously been demonstrated to exhibit exceptional optoelectronic properties since graphene's high carrier mobility and broad-spectrum absorption is complemented by high optical absorption of monolayer TMDs owing to their direct bandgap.<sup>1</sup>

In this work we compare and discuss the characteristics of epitaxial MoS<sub>2</sub>/graphene heterostructures grown on substrates with different structural properties such as small and large terrace size graphene/SiC (Figure 1a and b) as well as self-standing Nano Porous Graphene (NPG). Growth has been performed by Chemical Vapor Deposition using Ar as carrier gas and MoO<sub>3</sub> and S precursors. A systematic investigation of the resulting heterostructures has been conducted by microscopy and spectroscopy as a function of the growth temperature and precursor fluxes. The morphology of MoS<sub>2</sub> layers has a very different evolution on diverse substrates. For instance, on NPG, MoS<sub>2</sub> forms a 2D wetting layer on graphene which evolves into rhombohedral crystals for large precursor fluxes or longer deposition times (Figure 1c).

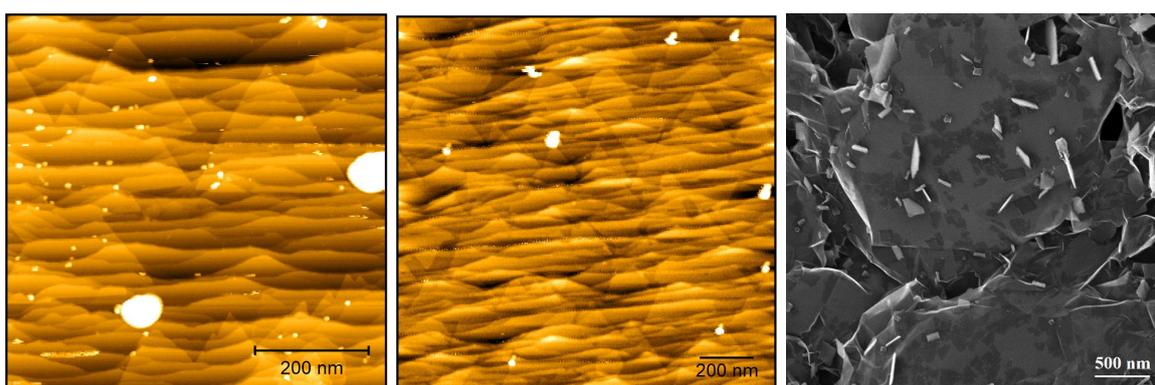


Figure 1: Atomic Force Microscopy images of MoS<sub>2</sub> grown on graphene/SiC with a) small terraces and b) large terraces. c) Helium Ion Microscopy image of MoS<sub>2</sub> grown on Nanoporous graphene.

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## **Brisbane – Poster Abstracts**

# Graphene-based materials for high performance Li-ion Capacitors (LICs)

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Lithium-ion capacitors (LICs) are hybrid devices combine a Li-ion battery (LIB)-type anode and a supercapacitor (SC)-type cathode in lithium-based organic electrolyte. LICs can provide high energy and power densities with long cycle life. However, LIB-anode materials suffer from sluggish reaction kinetics, which fails to match the fast-reaction kinetics of the SC-cathode. Moreover, SC-cathode materials usually have a relatively low storage capacity compared to the LIB-anode materials, resulting in a mismatch in the storage capacity between the anode and cathode<sup>1</sup>. We are developing new graphene-based materials with high specific capacities and fast reaction kinetics for LICs. I use holey reduced graphene oxide (H-rGO) as SC-type cathode and H-rGO-reduced Siloxene composite as a LIB-type anode. The preliminary results show that the prepared H-rGO has a BET surface area of approximately 286 m<sup>2</sup> g<sup>-1</sup> with pore size distribution ranging from ~1 nm to higher than 100 nm (Fig.1). When used as a cathode, a specific discharge capacity of ~ 38 mAh g<sup>-1</sup> was obtained at 0.2 A g<sup>-1</sup> with a capacity retention of 83% after 500 cycles.

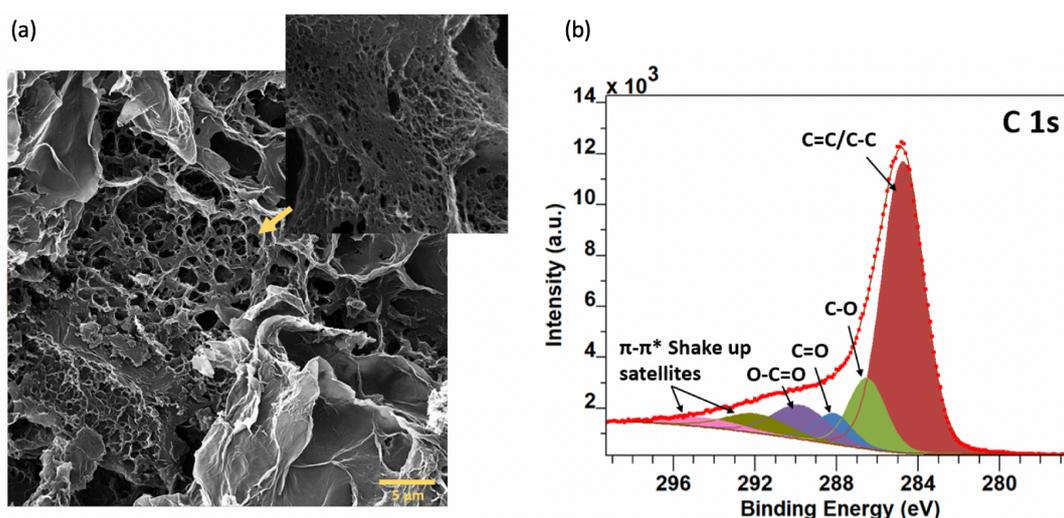


Fig.1 (a) HIM image and (b) high resolution XPS spectrum of C 1s for H-rGO.

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# Methylammonium carboxylate ionic liquid for the environmental-friendly processing of organometallic halide perovskite materials.

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The perovskite material is exhibiting promises in a broad range of application including solar cell, photodetector, light emitting diodes, pumped lasers and photocatalysts[1, 2]. However, the commercialization of perovskite potentially raises concerns about the environmental impact, since the solution-processing of perovskite material involves the employment of a range of noxious solvents such as Dimethylformamide, Dimethyl sulfoxide, Chlorobenzene and Toluene. As one of the key challenges toward commercialization of cheap and reliable perovskite, green chemistry for solution processable perovskite have to be addressed[3]. Herein, we demonstrate the capability of environmentally friendly methylammonium carboxylate-based protonic ionic liquid in perovskite material processing. Firstly, the ILs was shown to be an excellent medium for growing MAPbBr<sub>3</sub> nanocrystals (NCs), by which the NCs with different size, shape and strong photoluminescence up to 50% was synthesized thanks to the surface passivation effect of the alkyl carboxylate ligands. Secondly, when being used as an additive for fabrication of MAPbI<sub>3</sub> thin film, the ILs additive significantly enhance the film morphology, with the grain size increase from 100-300nm up to micrometre size. As a result, the fabricated MAPbI<sub>3</sub> PSC power conversion efficiency was enhanced from 14.05% to 16.32%. Furthermore, in synthesis of inorganic perovskite, the employment of methylammonium acetate ILs enable the formation of cubic phase CsPbI<sub>3</sub> in ambient condition. Our result provides a new avenue for environmental-friendly solution processing perovskite materials, which is critical for commercialization of perovskite based technology.

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## **Piezo-supercapacitors for Self-Powered Wearables and Medical Implants**

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Presenter - Sagar Jadhav - [sagar.jadhav@hdr.qut.edu.au](mailto:sagar.jadhav@hdr.qut.edu.au)

In the modern world, the energy requirements are growing exponentially with increase in number of electronic gadgets, wearable and medical electronics. Harnessing energy from natural phenomena and non-conventional sources such as mechanical motion is one of the promising approaches to power s devices. Piezoelectric material shows a great promise to effectively convert mechanical energy into electricity. A large amount of wasted energy could be put on to work if all the physical motions of living and non-living things can be effectively converted to electricity. The generated energy is required to be stored for its use as per the requirement. Piezo-supercapacitors is an emerging technology, which is an integrated system of piezoelectric and supercapacitors. Use nanomaterials can improve the performance of these integrated devices, to meet market requirements as power sources. Such devices can prove to be an excellent choice for application in wearable and medical implants, where the energy produced from body motions can be used for charging, making them self-sufficient devices.

# Formation of double emulsion for the encapsulation of liquid contents

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Accurate control on monodisperse core/shell droplets generated in a microfluidic flow-focusing device is vital for applications in various fields such as environment, biomedical, and food industry. In this work, we experimentally studied flow-focusing microfluidic devices allowing for fine-tuning the dimension of core/shell droplets. The dimension of the core/shell droplets was controlled passively based on the channel geometry and liquid phase flow. We used two PDMS devices with different geometries with three cross junctions to generate core/shell droplets (Figure 1(a)). The width of channels in one device is twice the other. The droplets consist of a HFE7500 fluorinated oil core and a polymer shell made of trimethylolpropane trimethacrylate (TMPTMA). Our experiments demonstrate that the dimension of the core and core/shell droplet increases, and the shell thickness gradually decrease in both devices as the oil flow rate increases from 60  $\mu\text{L/hr}$  to 140  $\mu\text{L/hr}$  while keeping other flow rates fixed. On the other hand, increasing the flow rate of the polymer from 130  $\mu\text{L/hr}$  to 190  $\mu\text{L/hr}$  resulted in the linear reduction in both radius of the core and the core/shell droplets in both devices. Subsequently, the thickness of the shell increased. Besides fluid flow rates, the channel width also affects the droplet generation. Figures 1(b, c) show that the wider channels result in a bigger core and a thicker shell layer. Optical and electron microscopy indicated that the geometry of the core/shell droplets remains unchanged as compared to the double emulsion droplet after solidification, drying and collection. These highly controllable microparticles have potential use in many fields such as the encapsulation, storage and delivery of lipophilic ingredients.

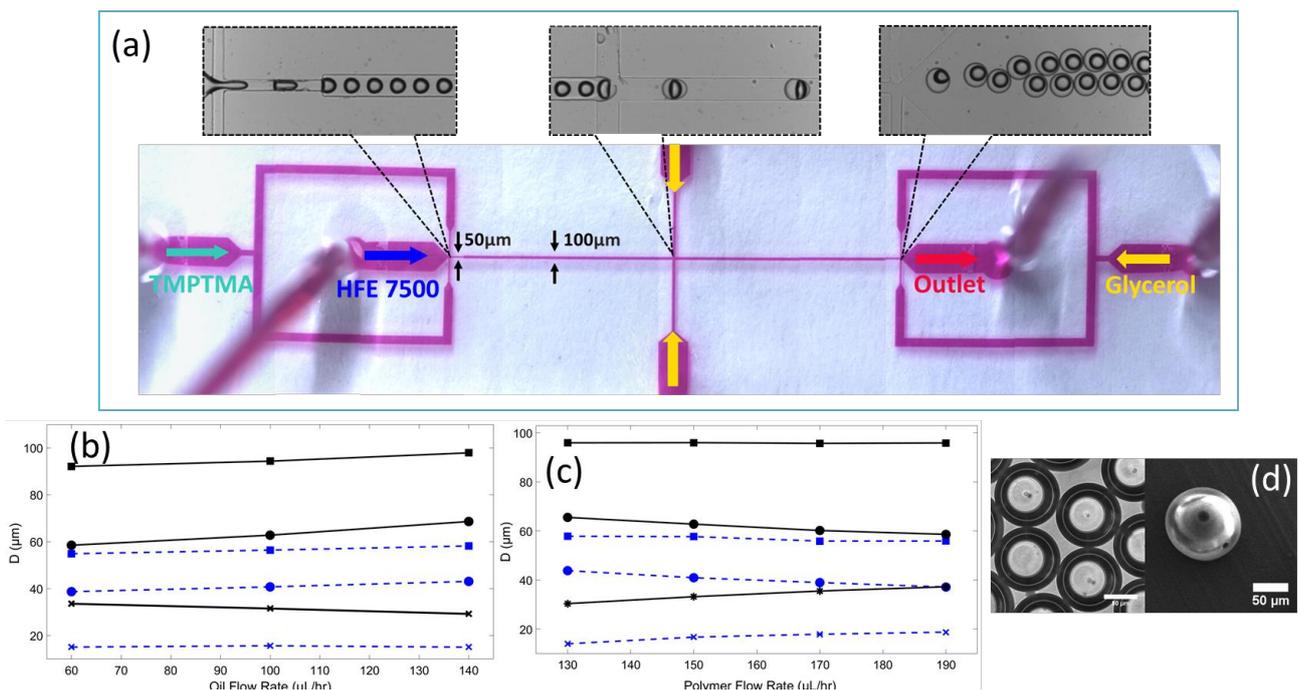


Figure 1. a) Photograph of PDMS microfluidic device with three cross junctions; Influence of oil and polymer flow rates on the core and core/shell droplet size as well as on the shell thickness: (b) impact of the oil flow rate; (c) impact of the shell flow rate.  $\bullet$  radius of the core droplet  $\blacksquare$  radius of the core/shell droplet,  $\star$  shell thickness, - - - microfluidic device I, — microfluidic device II with double wide channels; d) Microscopic images of core/shell droplets.

## **Interactions between coarse and fine galena and quartz particles and their implications for flotation in NaCl solutions**

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In this study, we have investigated the interactions between coarse and fine galena and quartz particles and their implications for flotation in NaCl solutions. Tested were four different galena/quartz particle systems: Coarse galena/Coarse quartz, Coarse galena/Fine quartz, Fine galena/Coarse quartz and Fine galena/Fine quartz. The experiments were carried out using a Hallimond tube, in NaCl concentrations of 0.01 M and 0.1 M, at pH 9. Our results showed the highest galena recovery for the Coarse/Coarse particle system, while the lowest galena recovery was reported for the Fine/Fine particle system. The findings also indicated a higher galena recovery for the higher NaCl concentrations.

The micro-flotation experiments on the mixed galena/quartz particle systems suggested that the recovery of galena could be affected by the size of the quartz particles making up the feed. It was shown that if the size of the quartz particles was increased, the recovery of fine galena particles improved.

Our results were discussed in terms of the competitive ion binding described by the chemisorption models for galena, quartz and air bubbles, as well as illustrated by the theoretical models representing the total interaction free energy as a function of the separation distance for each test condition. It was found that for all particle systems, galena/quartz interactions are dominated by repulsion. The interaction between two galena particles indicate attraction as the dominating force, while the interactions between the two quartz particles show repulsion in 0.01 M NaCl, which changes to an attraction with an increase in NaCl concentration. Galena/air bubble interactions are controlled by the repulsive electrostatic interactions in 0.01 M NaCl but become attractive in 0.1 M NaCl salt solution. On the other hand, the quartz/air bubble interactions are always repulsive, irrespective of the NaCl concentration.

Based on these theoretical predictions, we postulate that galena recovery is likely driven by a stronger attraction of the air bubbles towards the galena particles whilst the quartz/ air bubble interactions are dominated by repulsion.



## **Green technology a potential sustainable alternative for separation process of high-quality lignin and cellulose.**

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Sustainable development is a measured approach of the researchers, especially considering fossil energy consumption by industries to produce energy, thereby leads to CO<sub>2</sub> emission. Industries are the primary sector which contributes to a greater extent towards the emission of greenhouse gases. Among the other industries, paper and pulp industry trying to achieve a reduction of 80% CO<sub>2</sub> emission. Therefore, to achieve the goal, biomass fractionation and paper recovery treatment need a revolutionary change. Newly introduced Deep Eutectic Solvents (DES) composed of naturally obtained primary metabolites such as sugars, amino acids and organic acids. DESs are environmentally suitable, recyclable, low-volatile and cost sufficient as well as can operate at low temperatures and pressure. DES has the strong ability to donate and accept the electrons or protons which makes them ideal chemical for the degradation process of a range of components such as sugars, polysaccharides, salts, drugs, proteins and amino acids. Eutectic mixture of urea and choline chloride was first discovered in 2005, primarily for electrochemical application, since then scientist has been finding applicability in different field of study. Implementing the use of DES in paper industry will allow in achieving the sustainable pulping process by fractionation of lignin from biomass, efficient technique to dissolve cellulose. The study aims to develop a green chemical to isolate the pure form of cellulose from a paper by dissolving the contaminants. Furthermore, examining the isolated cellulosic fibres having good tensile strength as well as keeping a balance between ecological and economic feasibility of the green chemical delignification process.

# Behaviour of the liquid marble shell at different core liquid surface tension

Pradip Singha<sup>1</sup>, Nhat-Khuong Nguyen<sup>1</sup>, Nam-Trung Nguyen<sup>1</sup>, Chin Hong Ooi<sup>1</sup>

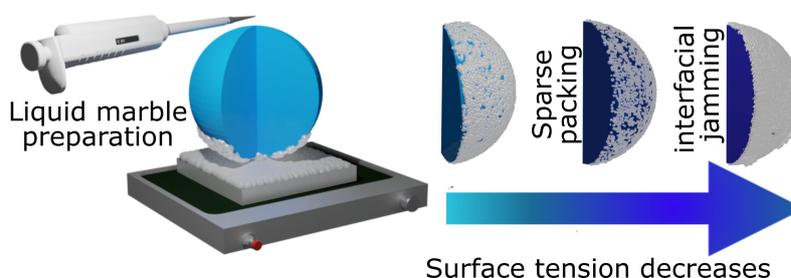
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Liquid marble, as an emerging platform for digital microfluidics, has shown its potential in biomedical applications, cosmetics, and chemical industries. Unique features such as low evaporation rate, low friction, and a porous shell enable liquid marble to be a potential tool for gas sensing, cell culture, and drug delivery. With the growing interest in liquid marbles in these fields, it is important to understand the structure of the liquid marble shell and how it behaves with the variation of the surface tension.

A liquid marble shell dominates its macroscopic properties. The behaviour and the structure of the shell depend on the properties of encapsulating particles, properties of the core liquid, and the preparation method. In this work, we studied the behaviour of the liquid marble shells at different core liquid surface tensions. Systematic observation of the liquid marble shell at different surface tensions indicated that the shell thickness decreases with the surface tension.<sup>1</sup> Surfactant mediated surface tension reduction allows the encapsulating particles to penetrate more into the core liquid and decrease the shell thickness. Interestingly, the thickness of the shell increases with a further decrease of the surface tension. This phenomenon is attributed to the interfacial jamming of the encapsulating particles at lower surface tension.

This work could provide a new insight to understand the contribution of the encapsulating particles to the macroscopic properties of a liquid marble, which are likely to benefit liquid marble-mediated micro reaction and cell culture.



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## **Melbourne**

10/2/21 – 11/2/21

## **Melbourne – Keynote Abstracts**

## **Characterization of physically robust hydrogels for biomedical applications**

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

### **Biography**

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

### **Abstract**

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

## Using microfluidics to probe complex flows in biomimetic systems

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

### Biography

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

### Abstract

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

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

## Multifunctional Interfaces from Nature's Versatile Lubricant

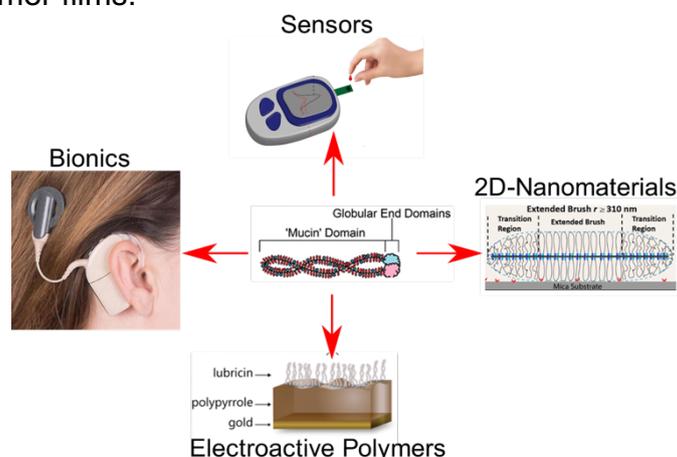
Dr George (Wren) Greene, Institute for Frontier Materials and ARC Centre of Excellence for Electromaterials Science, Deakin University, Melbourne, Victoria 3216, Australia

### Biography

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

### Abstract

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



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

A/Prof. Valeria Garbin, Department of Chemical Engineering, [Delft University of Technology](#)

### **Biography**

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

### **Abstract**

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

## **Melbourne – Oral Presentation Abstracts**

# Metallo-nanodroplets for catalysis and nanostructure fabrication

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

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

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

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## Carboxylated nanocellulose superabsorbent for retaining soil water

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

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

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

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

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

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

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

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

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

## Deep eutectic solvents for cryopreservation

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

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

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

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

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

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## Abstract

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

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

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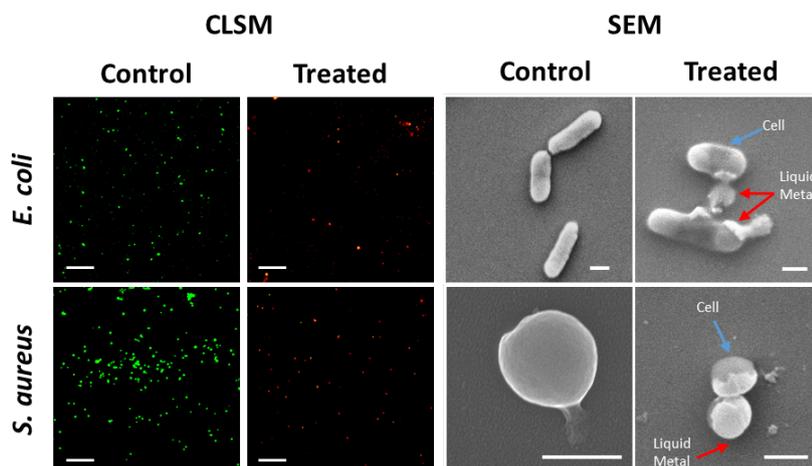
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# Antibacterial Gallium Liquid Metal Micro-/Nanodroplets

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



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

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

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*Introduction:* Digestion of the milk lipids in our intestines yields monoglycerides and fatty acids that self-assemble into a variety of liquid crystalline structures. This self-assembly process is species dependent,[1] suggesting an important role for these structures in infant nutrition. Our recent work has focussed on designing lipid mixtures that replicate the self-assembly of different natural milks during digestion and analysing how the self-assembled digestion products interact with biliary emulsions to influence nutrient activity.

*Methods:* Lipid mixtures were prepared by mixing either purified homotriglycerides or cow milk fat and canola oil. These lipid mixtures were dispersed to form milk-like emulsions or canola oil was mixed directly with cow's milk to generate milk-like emulsions. Coherent anti-Stokes Raman spectroscopy (CARS) microscopy was used to confirm mixing of the lipids into cow's milk and Small angle X-ray scattering with *in situ* lipolysis was used to measure the self-assembly of lipids in emulsions of the mixed lipids during digestion.[2,3]

*Results & Discussion:* The triglyceride composition of the digesting emulsions was found to be a primary driver of lipid self-assembly during milk digestion. By designing emulsions with the right balance of medium/long chain saturated lipids (more abundant in cow's milk) and long chain unsaturated lipids (more abundant in human milk), lipid mixtures could be produced that replicated both natural milks and infant formulae. The lipid self-assembly in mixtures of cow's milk and canola oil was found to replicate that of human milk when the right balance of these lipids was struck, irrespective of whether the lipids were pre-mixed and emulsified or whether the canola oil was dispersed directly into cow's milk. These mixtures provide simplified lipid compositions that can be used as milk mimics with tuneable colloidal structures to investigate the interactions of endogenous surfactants, lipophilic drugs and nutrients with milk in the gastrointestinal tract.

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## **The shape, size and diffusion of anisotropic nanoparticles near interfaces**

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

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

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

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

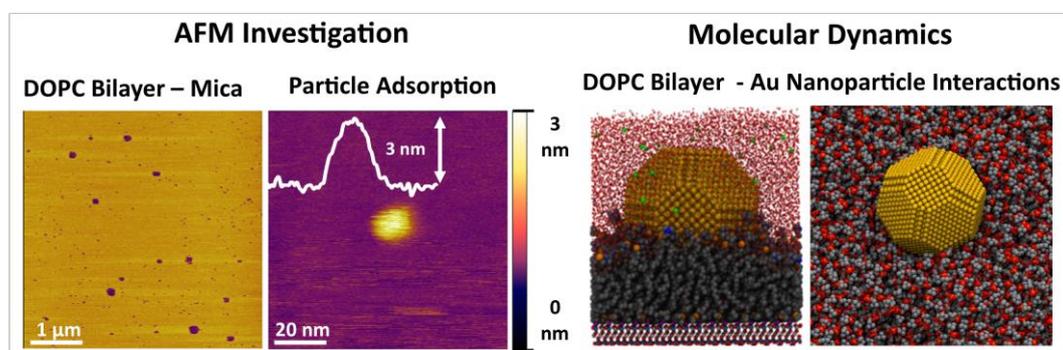


Figure 1. AFM and Molecular dynamics simulation investigation of the interaction of 5 nm AuNPs with a supported DOPC lipid bilayer formed at a mica surface.

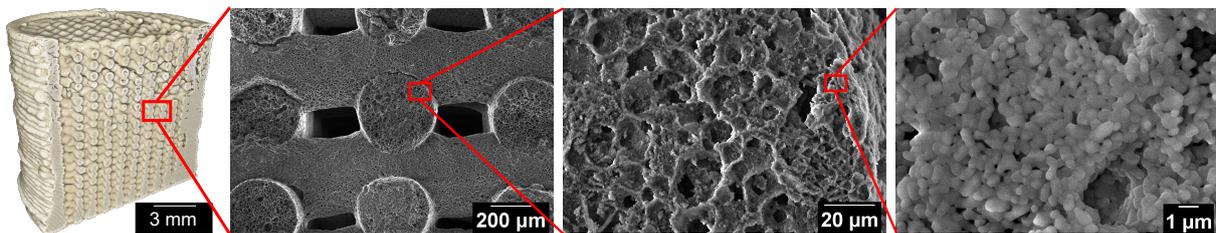
# 3D printing with colloidal particle pastes using aqueous suspension-oil formulations

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



Multiscale structure produced in alumina.<sup>1</sup>

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# Quasiperiodic Light

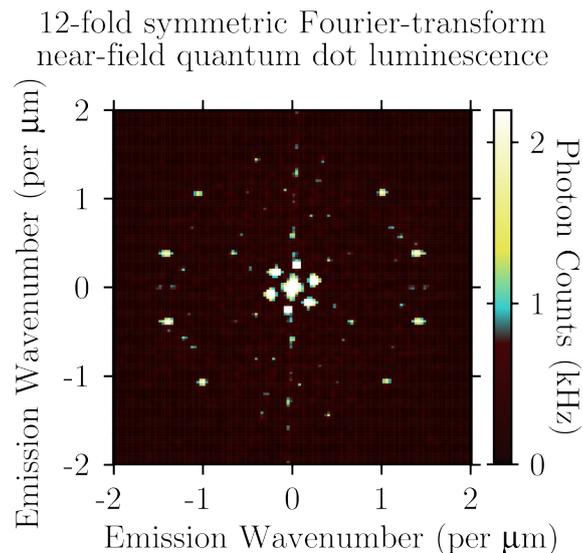
Laszlo Frazer<sup>1</sup>, Thomas M. Mercier<sup>2</sup>, Chirenjeevi Krishnan<sup>2</sup>, Zhou Xu<sup>3</sup>, Amelia Liu<sup>4</sup>, Gangchen Yuan<sup>1</sup>, Pavlos G. Lagoudakis<sup>5</sup>, Martin D. B. Charlton<sup>2</sup>, Alison M. Funston<sup>1</sup>

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

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



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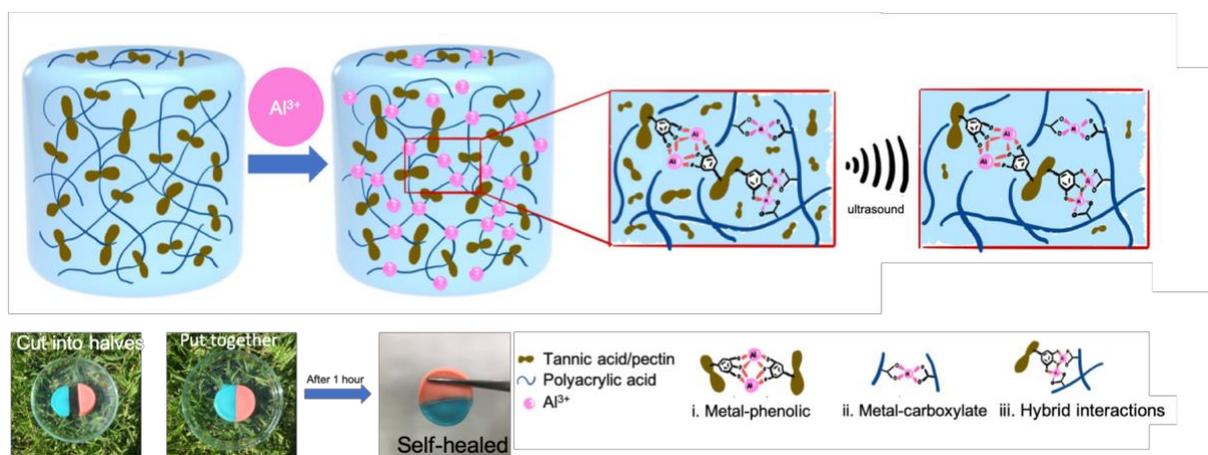
# High-water-holding pectin-based robust hydrogels with self-healing, biocompatible and anti-bacterial properties for drug-delivery

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



## Solvent effects of protic ionic liquids on proteins

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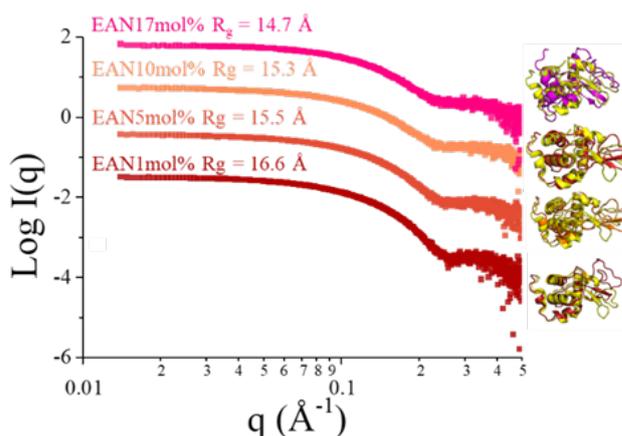
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Protic ionic liquids (PILs) are cost efficient “designer” solvents which can be tailored to have properties suitable for a broad range of applications. PILs are also being combined with molecular solvents to enable more control over the solvent environment,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



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

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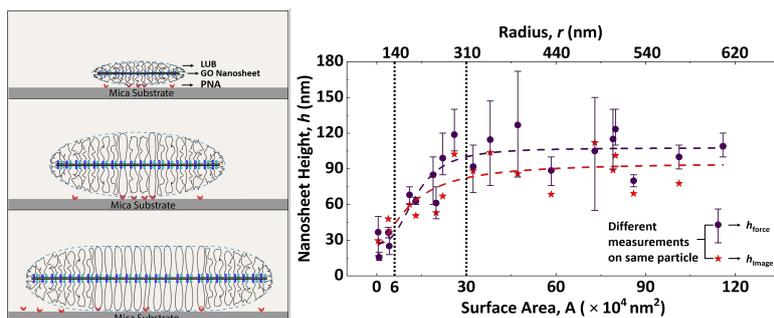
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# Self-Assembly of Lubricin (PRG-4) Brushes on Graphene Oxide Affords Stable 2D-Nanosheets in Concentrated Electrolytes and Complex Fluids

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



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

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

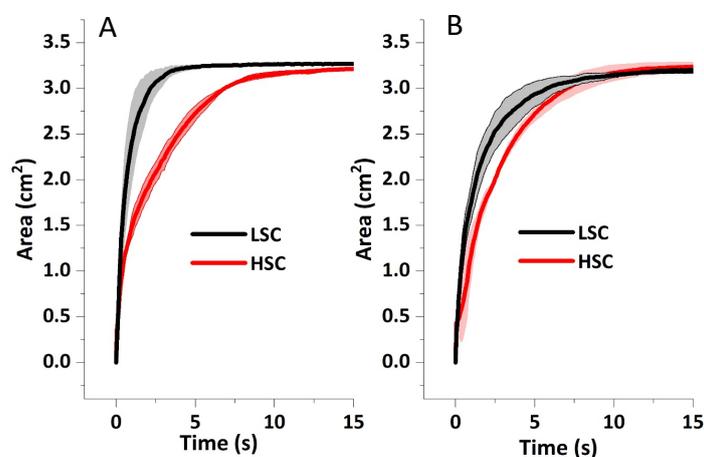


Figure 1: Effect of surface charge on absorbed area over time for LSC and HSC nanocellulose foams (A) milli Q water and (B) 0.9wt% NaCl.

## **Droplet Microfluidic SANS for interfacial coatings of soft matter systems**

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

# Investigating the Spatially Dependent Properties of Plasma Polymerised Acrylic Acid Films

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

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

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

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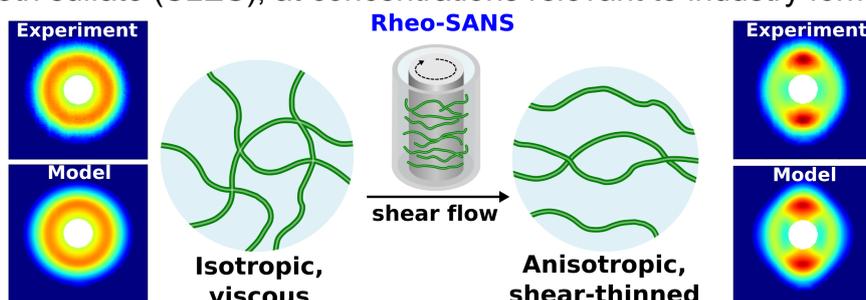
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Wormlike micelles (WLMs) are self-assembled, thread-like surfactant aggregates that, at sufficiently high concentrations, entangle to form a highly-viscous mesh. Above a critical shear rate, this mesh disentangles and aligns with the direction of flow,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



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

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

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

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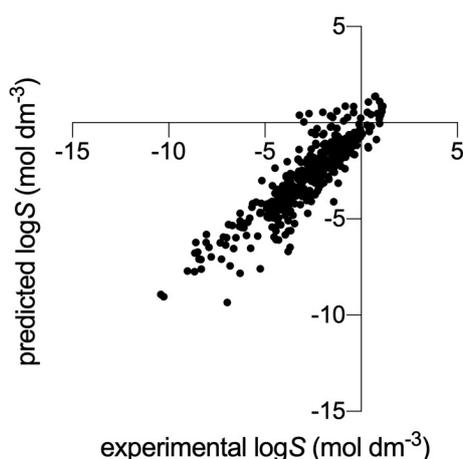
# Predicting aqueous solubility by QSPR machine learning modeling

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



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

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

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

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

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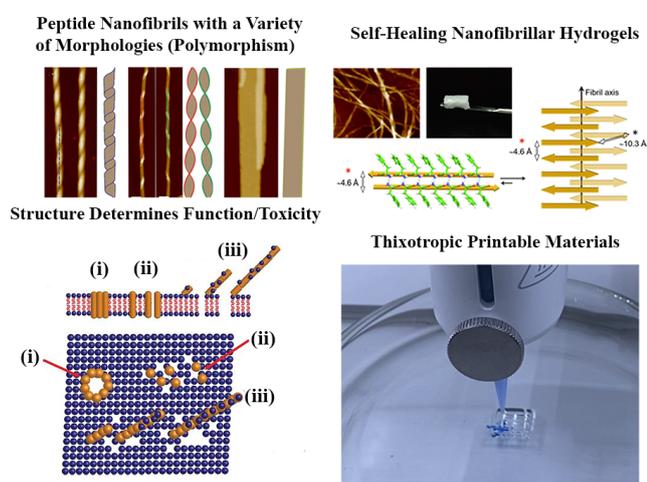
# Investigating the self-assembly of short peptides: From amyloid disease to bioprinting

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



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

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

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

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

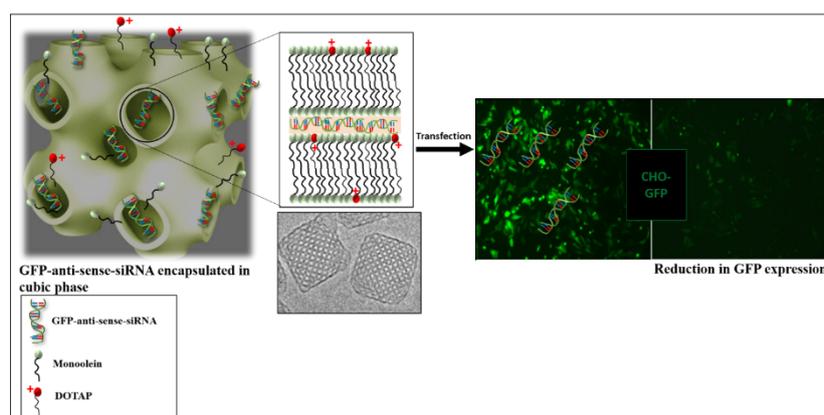


Fig 1. Cationic-cubosome mediated GFP-anti-sense-siRNA delivery into the CHO-GFP cell

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## Polarisation engineering through polymer-nanomaterial interfaces

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

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

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

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

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## Crusty Scum Model

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

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

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## Low density metal core-shell particles for liquid marble formation

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

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

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# Surfactant-free techniques for nanoparticle deposition using hydrotropes

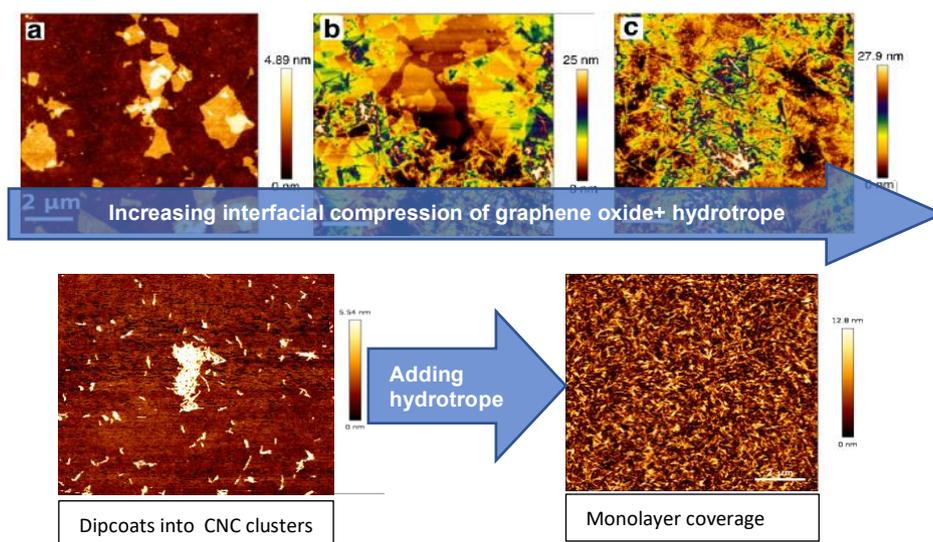
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When nanomaterials such as graphene oxide nanosheets or cellulose nanocrystals adsorb to the air-water interface, they can be transferred to a substrate through dipcoating, imbuing the substrate with their characteristics. Surfactants are often added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

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



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# Ultrasound-assisted fabrication of red blood cell ghost “bubbles”

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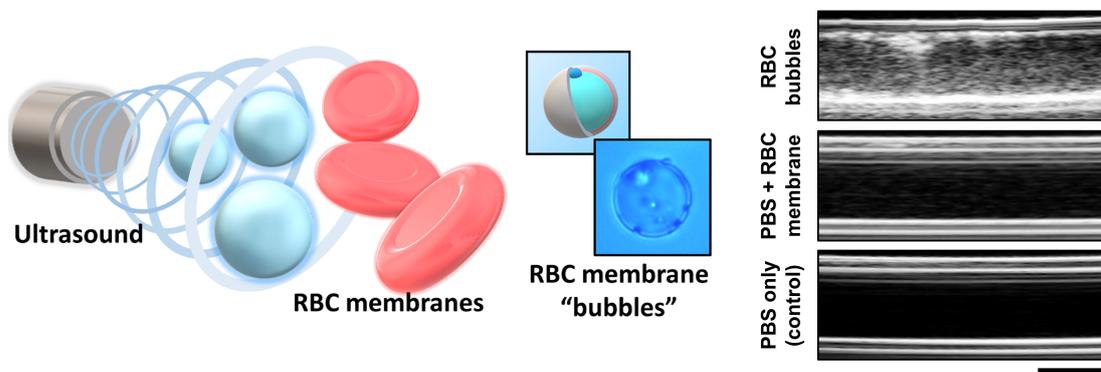
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Ultrasound imaging is a non-invasive, relatively inexpensive, real-time, diagnostic imaging technique with a broad application range that can complement other structural and functional imaging modalities. However, this technique is limited by the low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

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



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

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

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

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

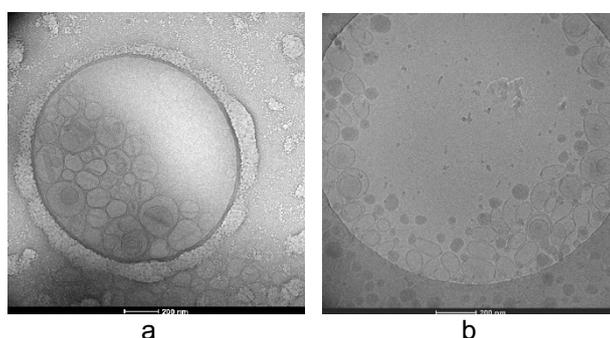


Figure 1 a) Elongated liposomes were successfully prepared with encapsulated drug nanocrystals; b) Elongated shape was maintained in the final polymeric nanocapsules

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

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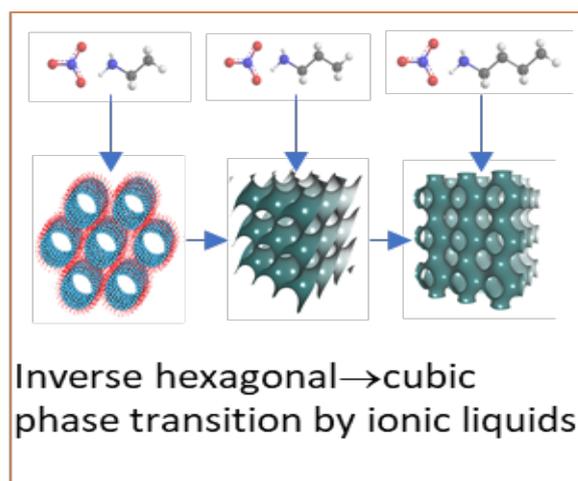
## Tuning nanostructured lyotropic liquid crystalline mesophases in lipid nanoparticles with protic ionic liquids

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



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

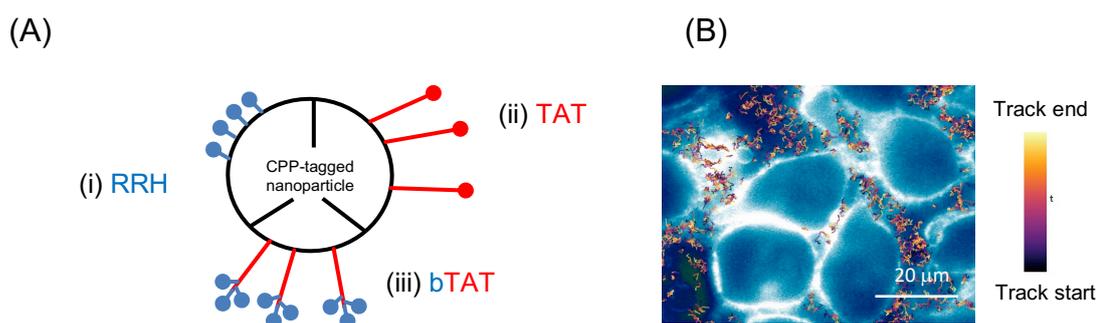
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Effective delivery of therapeutic compounds remains limited by our understanding of interactions between drug carriers at the nano-bio interface. Cationic cell penetrating peptides (CPPs) are reported to enhance the cellular absorption of therapeutic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

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



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

## **Melbourne – Poster Abstracts**

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

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

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

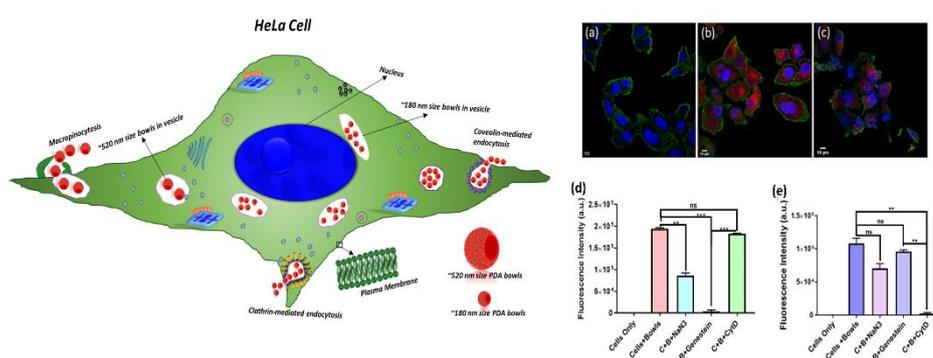


Figure 1. (A) Schematic diagram of size-dependent cellular internalization of PDA bowls. Confocal images (a to c), (a) only cells, (b and c) cells after incubation with ~180 nm and ~520 nm size PDA bowls for 24 h. Fluorescence intensity analysis of inhibitor treated and non treated HeLa cells after incubation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

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

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

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

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**Objectives:** Colostrum contains lipids and bioactive proteins that can stimulate the development of organs and prevent diseases in infants.<sup>1</sup> Surprisingly there have been no reports of colostrum being assessed in the context of lipid digestion, which is critical in the transport of lipophilic nutrients. Hence, this project aims to understand the differences in the self-assembly of lipids during the digestion of human colostrum and emulsified colostrum-mimicking lipid mixtures and the potential interactions with bioactive proteins.

**Methods:** Human colostrum samples were digested under intestinal conditions. The *in vitro* digestion model was coupled to small-angle X-ray scattering at the Australian Synchrotron, enabling acquisition of phase formation as a function of extent of digestion.<sup>2</sup> Emulsified colostrum-mimicking lipid mixtures were formulated by weighing known amounts of triglycerides and dispersing the lipids with a buffer.

**Results & Discussion:** Prior to digestion, a lamellar phase was present in human colostrum caused by the formation of calcium soaps due to self-digestion by the breast milk's own bile salt-stimulated lipase (BSSL). In contrast, a lamellar phase was not evident in the emulsified colostrum-mimicking lipid mixture before the start of digestion due to the absence of BSSL and only grew once digestion was initiated. However, a cubic phase was observed as digestion progressed for the emulsified mixture, but not human colostrum. *In situ* monitoring of the lipid liquid crystalline structures formed during the digestion of emulsified colostrum mixture revealed additional phases formed due to differences in extent of digestion as compared to human colostrum. Further studies to increase extent of digestion such as including bile salt micelles and consequent interaction with bioactive proteins will elucidate the role of lipid structuring in the overall function of human breast milk.

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

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

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

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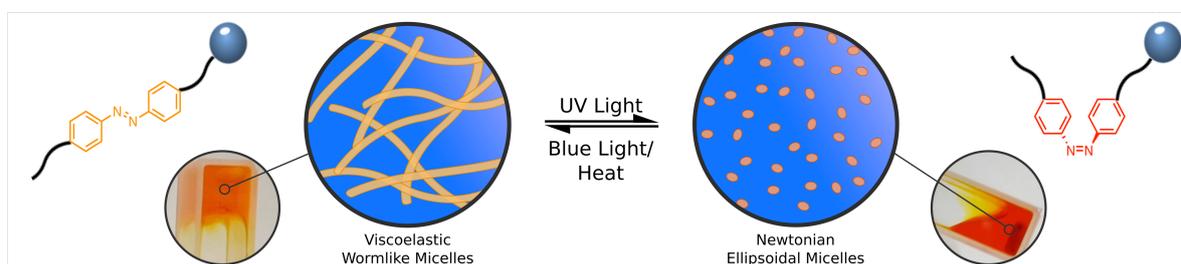
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Photo-rheological fluids (PRFs) are materials that modulate their flow properties, such as viscosity and elasticity, when exposed to light of a specific wavelength. The unique stimulus-responsive properties of PRFs, driven by control of nanoscale surfactant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

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

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



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## **New insights into colloidal phase transitions using neutron scattering techniques**

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

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

## Exploring the nanostructure of a deep eutectic solvent at solid interfaces

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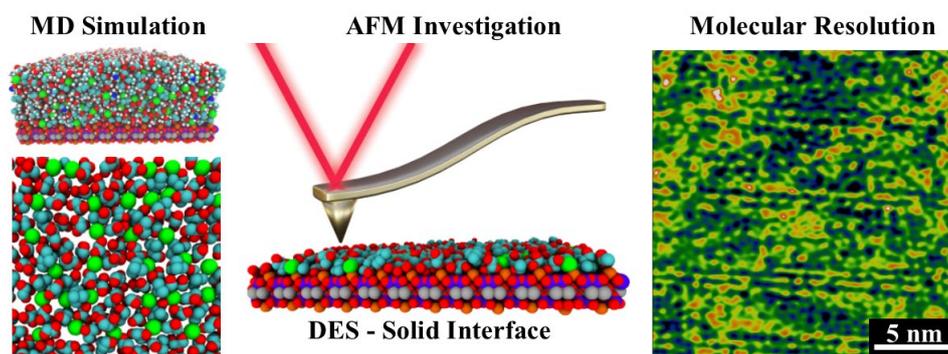
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Deep eutectic solvents (DESs) are an attractive class of tuneable solvents for electrochemical systems, materials chemistry, catalytic processes, and chemical extraction.<sup>1,2</sup> To date, the study of deep eutectic solvent nanostructure has largely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

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



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

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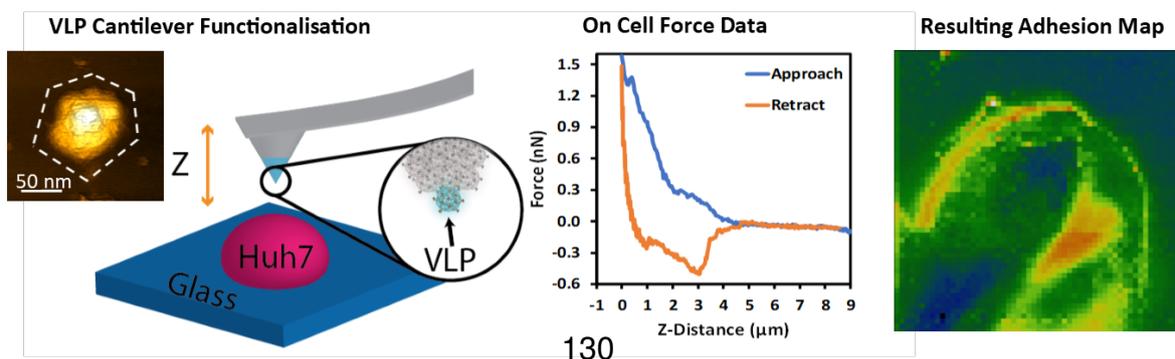
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Recent studies are changing the way researchers approach utilizing cell culture systems to address complex research questions. For example, cell cultures have been successfully used to study hepatitis C virus (HCV) for many years. However, most work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



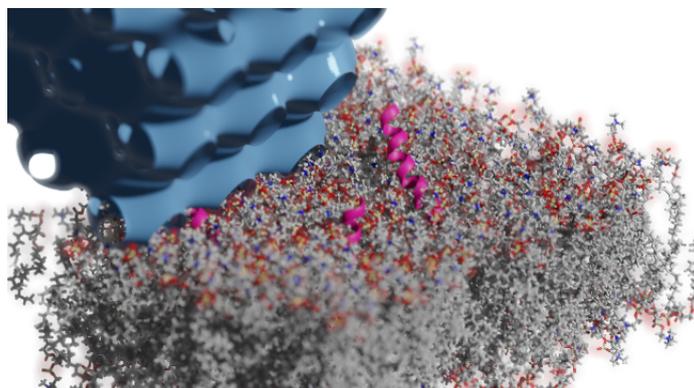
## Delivery of antimicrobial peptides to model membranes by cubosome nanocarriers

Brendan P. Dyett<sup>1</sup>, Haitao Yu<sup>1</sup>, Biserka Ladic<sup>1</sup>, Nilamuni De Silva<sup>1</sup>, Anthony Dahdah<sup>1</sup>, Lei Bao<sup>2</sup>, Ewan W. Blanch<sup>1</sup>, Calum J. Drummond<sup>1</sup>, Charlotte E. Conn<sup>1</sup>

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



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

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

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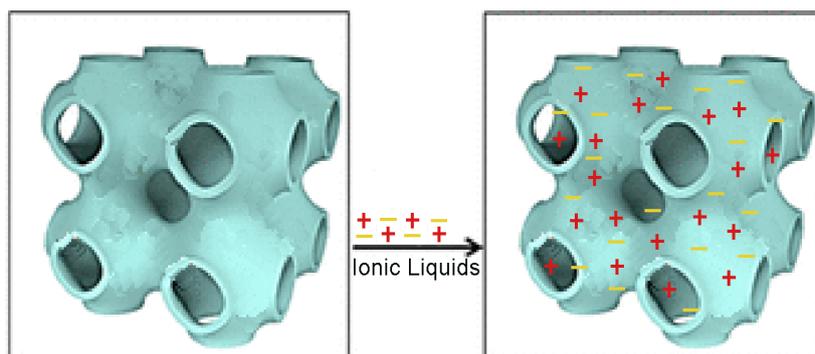
## Formulation and characterization of lyotropic liquid crystalline lipid nanoparticles in designer ionic solvents

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



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

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

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

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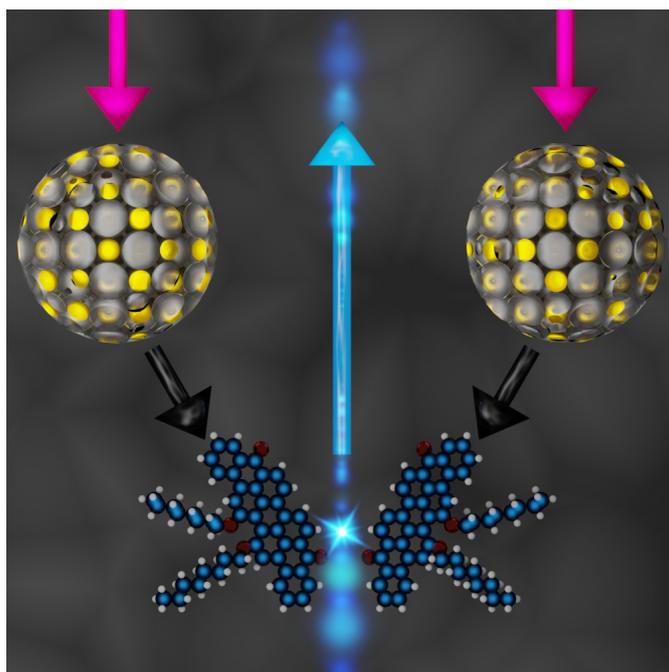
# Optimal quantum dot size for sensitizing photovoltaics with fusion

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



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

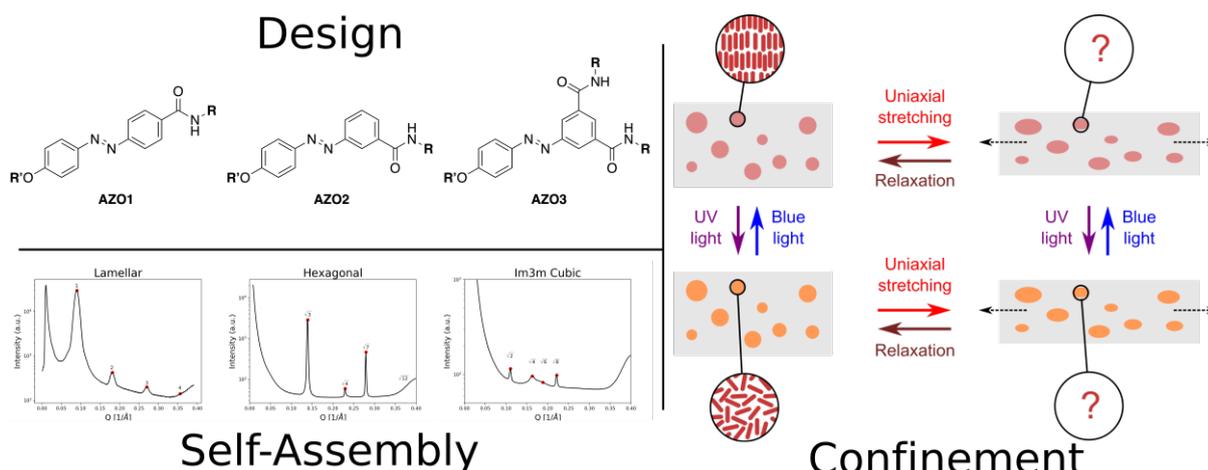
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The azobenzene functional group is known to have a facile and reversible photo-induced *E/Z* isomerization. By incorporating this functional group into molecules, materials that exhibit light-induced changes in their chemical or physical functionality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

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



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

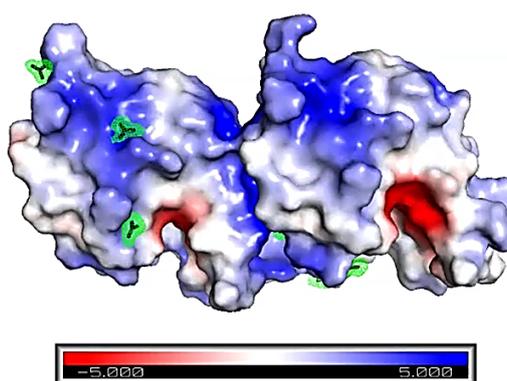
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Ionic liquids (ILs) are liquids that are comprised entirely of ions<sup>1</sup>. IL solutions have been widely studied for biochemical applications in recent decades. IL ions interact with proteins, and can profoundly regulate their properties and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

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



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## Drying Fronts in Blood Droplets

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

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

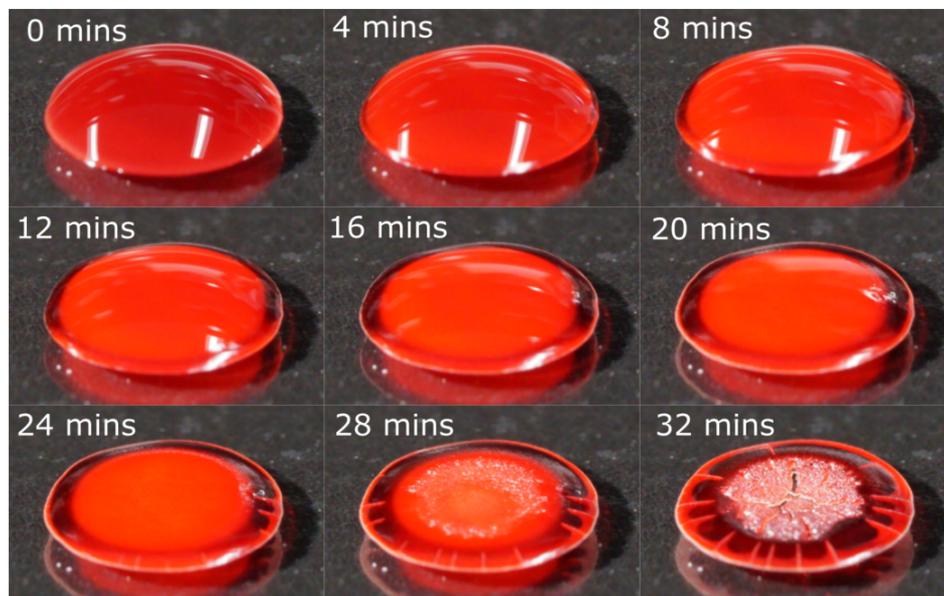


Figure 1. Whole blood from a healthy donor drying on microscope glass

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## Drug Resistant Pathogens are Susceptible to Silver Coated Nanotextured Titanium Surfaces

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

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

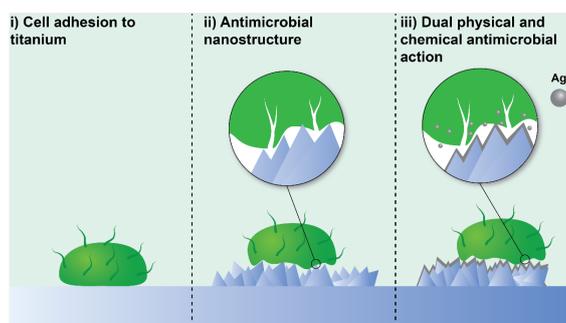


Figure 1. Schematic illustrating the i) normative cell adhesion to a titanium surface, ii) physico-mechanical puncture of microbial cells on a nanotextured surface, iii) a dual physical and chemical mode of antimicrobial action.

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

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

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

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

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

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

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

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

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

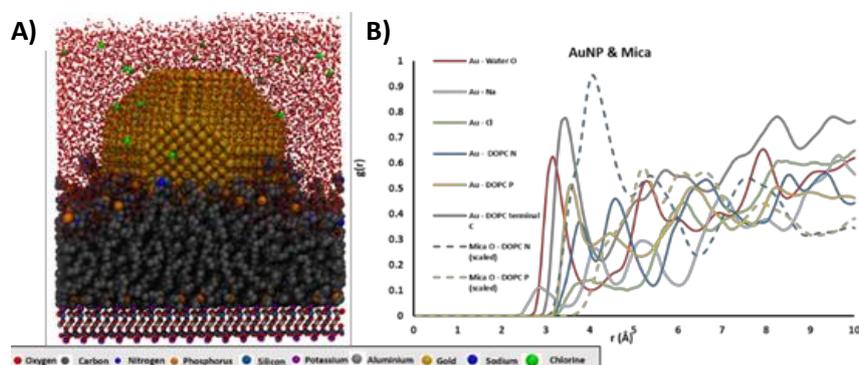


Figure 1. Molecular dynamics simulations of 5 nm Au Nanoparticle adsorption to a DOPC lipid bilayer formed at a mica surface. A) Simulation snapshot. B) Radial distribution data.

# **Influence of electrolytes on the coalescence of free droplet collisions**

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

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

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

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

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

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

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

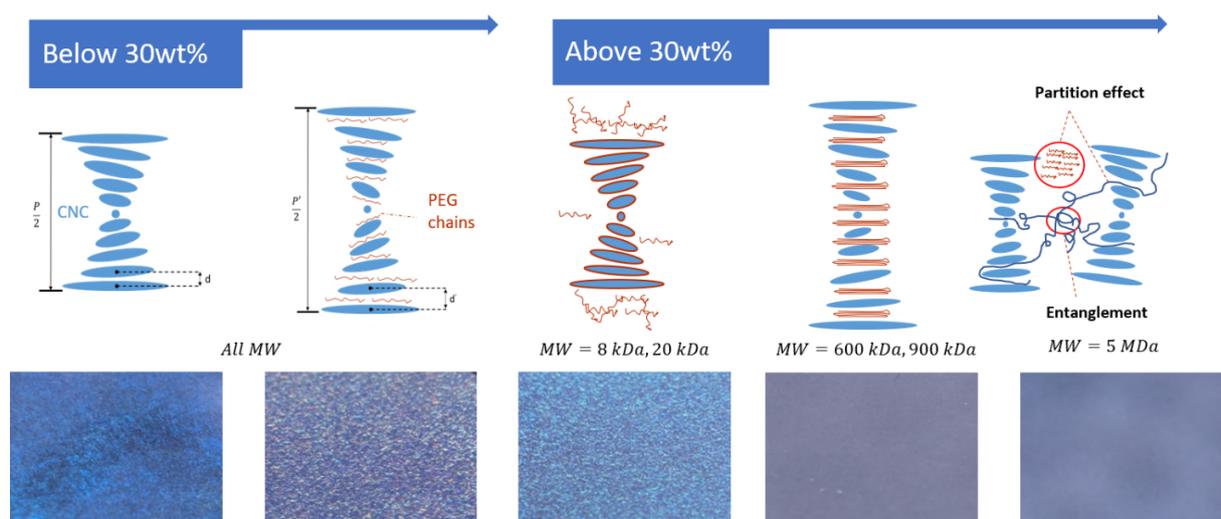
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Cellulose nanocrystals (CNC) can produce photonic composite films that selectively reflect light based on their periodic cholesteric structure. Flexible free-standing composite films of CNC incorporating poly(ethylene glycol) (PEG) of five different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



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

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

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

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

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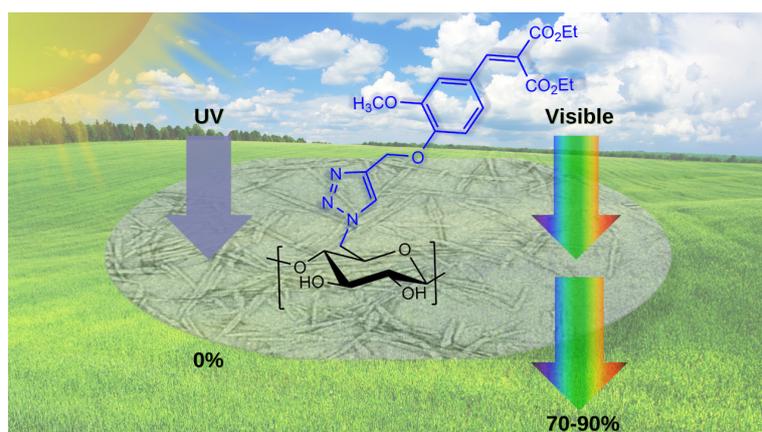
# Phenolic ester-decorated cellulose nanocrystals as anti-UV reinforcement nanofillers in polyvinyl alcohol films

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



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

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Lyotropic liquid crystalline (LLC) lipid nanoparticles have gained attention as drug delivery systems due to their ability to carry a wide range of hydrophobic and hydrophilic drugs. Among others, cubosomes, with an internal bicontinuous cubic ( $Q_2$ ) structure, show fast drug release and more vital membrane interaction, in contrary, hexosomes ( $H_2$ ) exhibit much slower release profile (Figure 1)<sup>1</sup>.

In this study, we synthesised nine novel ionisable Aminolipids with tertiary amine-containing headgroup and formulated them in Monoolein (MO) / Pluronic based dispersions. We hypothesise that at physiological pH (7.4), the lipid headgroup charge is neutral, and the nanoparticles exhibit characteristics of slow release phases such as  $H_2$ . At lower pH (5.0-6.5), the headgroup is protonated with a positive charge, which drives the system to  $Q_2$  phase for faster drug release and stronger fusion with cancer cell membranes (Figure 2).

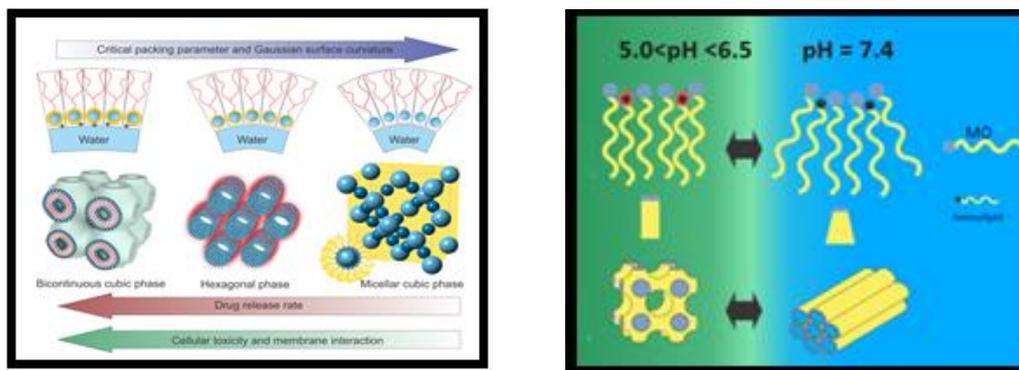


Figure1: Non-lamellar LLC phases and their properties      Figure2: Aminolipid incorporation to MO nanoparticles

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

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# Polymer-silica core-shell capsules for versatile copper extraction

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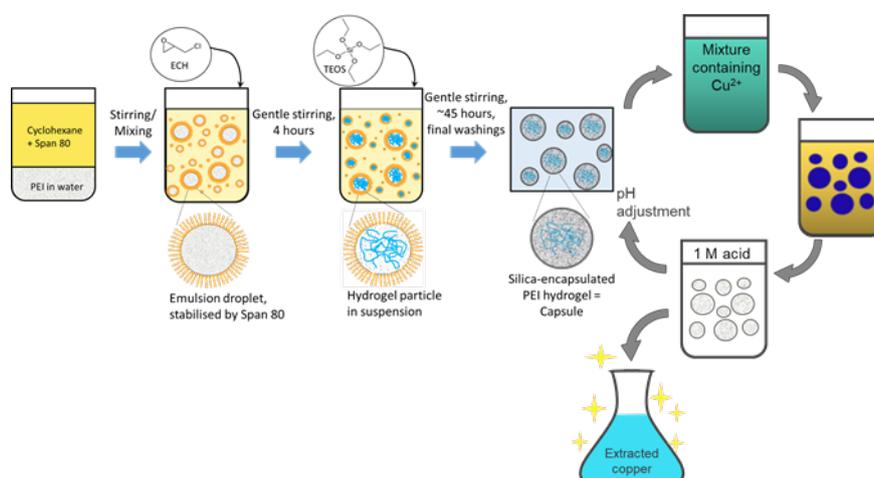
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The depletion of natural resources together with growing contamination problems cause a pressing demand for efficient refining/purifying methods and materials. For instance, the growing limitation of copper stocks concurrent with increased copper pollution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

In this study, employing a simple one-pot synthesis method,<sup>1</sup> polyethylenimine (PEI)/SiO<sub>2</sub> core-shell capsules were developed that act as highly efficient binding agents for copper, even in acidic conditions that are relevant to most cases corresponding to copper extraction. At the same time, the especially smooth surface of the silica shell provides a robust, inert protective coating, allowing use of these capsules in multiphase mixtures, such as concentrated sludges, mine tailings, soils and comminuted ores. The results demonstrate that capsules can be fully recycled to their original state by simple washing with 1 M acid, and thereby can be repeatedly used for copper extraction without loss of efficiency. The efficient synthesis, and extraction/recycling open up new opportunities for refining/purifying technologies in various sectors of industry.

## Synthesis of capsules and their use in copper extraction cycle.



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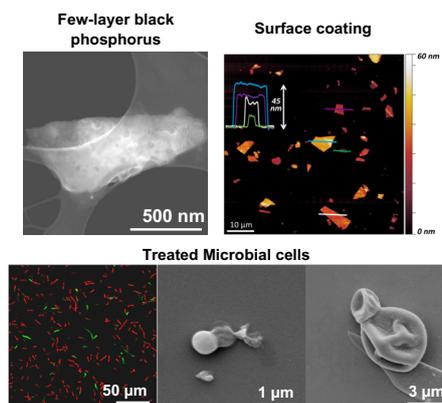
# Exploiting imperfections in few-layer black phosphorus for a broad-spectrum antimicrobial

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



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

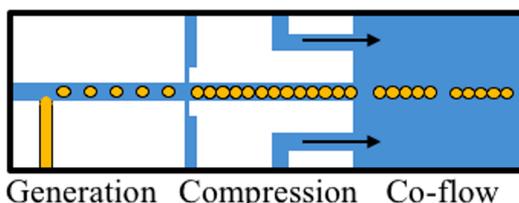
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The application of 3D-printing technology to fabricate microfluidic devices with sub millimetre channel dimensions has evolved as the 3D printer resolution has improved overtime. Compared to conventional fabrication process (e.g. photolithography and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

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



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## Understanding Polymer silica core shell micro composites

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

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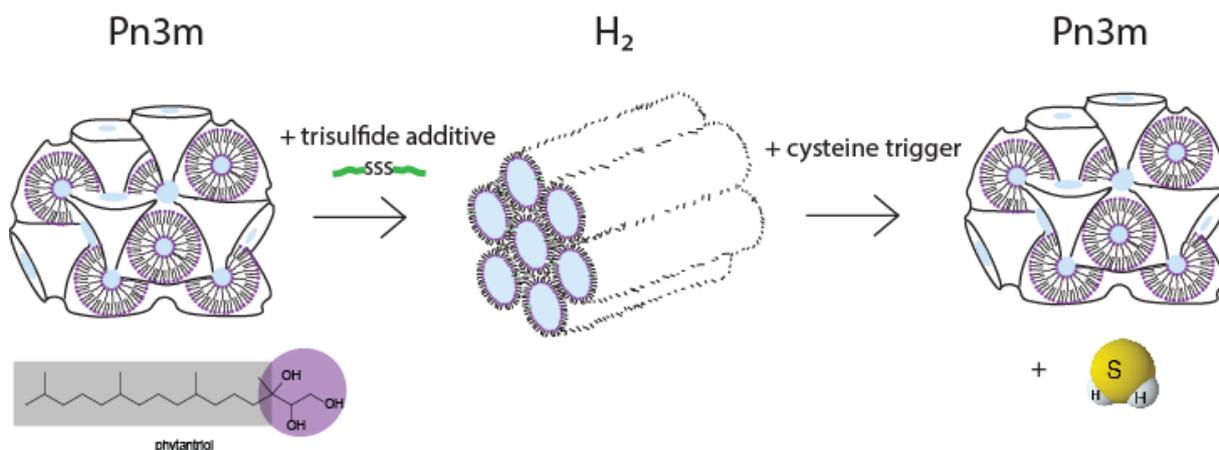
# Trisulfide amphiphiles as actuators to control phytantriol lipid self-assembly

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Stimuli-responsive nanomaterials are of increasing interest as researchers look to address drug delivery issues such as those associated with off-target effects. Our research focuses on lipid based nanostructured materials. These materials can be employed as biocompatible, multicompartmental matrices which can accommodate drug molecules with a wide range of physicochemical properties.<sup>1</sup> Manipulating environmental variables, such as temperature and pH, and the incorporation and activation of stimuli responsive molecules and nanoparticles, can enable switching between different liquid crystalline phases which in turn provides the opportunity to trigger and control the release of encapsulated material. In the current study we aimed to create thiol responsive lipid nanostructures by the incorporation of a thiol degradable trisulfide based amphiphile. Using synchrotron small angle X-ray scattering we found that the initial lipid phase formed was dependent on the concentration and structure of the additive. Furthermore, upon the addition of a thiol trigger we observed H<sub>2</sub>S release and in some cases an additional lipid phase change. The potential for thiol specific concomitant release of H<sub>2</sub>S and encapsulated material makes this approach attractive to formulation scientists looking for controlled drug release.



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## **Newcastle**

9/2/21

## **Newcastle – Keynote Abstracts**

# **From froth flotation on Earth to electrostatic beneficiation on the Moon: The route towards dry mineral processing**

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On Earth, froth flotation is a hugely successful process to separate minerals, consuming large quantities of water and producing vast amounts of tailings. On the Moon, the production of small quantities of oxygen or water in the next 5 years will mark a new era for human space travel. Although seemingly unlinked, the success of both flotation and lunar oxygen production is related to mineral surface properties. Furthermore, bringing together the space resources and mineral processing sectors brings a fresh perspective to our terrestrial operations, particularly with respect to water use. In this talk, we will look at methods of separating Moon dust based on electrostatic properties, and consider how this might enable the transformation of mineral processing from wet to dry.

## **Biography**

Dr Kathryn Hadler is a lecturer in the Department of Earth Science and Engineering at Imperial College London. Her primary field of research has been optimising froth flotation performance, particularly through numerous industrial experimental trials. In recent years, she has focused on the removal of water from mineral processing operations and the transition to dry processing on Earth, and the use of beneficiation techniques on the Moon. She leads the European Space Agency Topical Team on space resource utilisation.

## **Rational Design of Poly(ethylene glycol) Nanoparticles for Targeted Drug Delivery**

Jiwei Cui

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### **Biography**

Jiwei Cui is a professor in the Key Laboratory of Colloid and Interface Chemistry of the Ministry of Education at Shandong University in China. He received his Ph.D. in colloid and interface chemistry from Shandong University in 2010 and worked as a research fellow at The University of Melbourne during 2010-2016. He was awarded as an ARC Super Science Fellow in 2011 and was selected as a Young Talent Fellow in China in 2016. His research interests include colloidal assembly, interface engineering, polymer hydrogels, drug and vaccine delivery.

Robert Chapman

### **Abstract**

Successful accumulation of drugs specifically at diseased sites is mainly limited by biological barriers, especially the nonspecific uptake of drug carriers in mononuclear phagocyte system (MPS). Hence, it is critical to develop drug delivery systems that can specifically bind to diseased cells, while avoiding interactions with normal, healthy cells. This presentation will demonstrate the rational design of polymer particles mainly composed of poly(ethylene glycol) (PEG), and will show the cell association and biodistribution of these particles, as well as cell targeting of PEG particles modified with targeting molecules for drug delivery. The optimization of PEG particle engineering to overcome the MPS biological barrier for efficient tumour targeting in mouse studies is examined by tuning PEG molecular weight, particle size, particle stiffness, and targeting moieties, which highlights the influence of unique aspects of polymer particles on biological interactions. The reported PEG particles represent a new type of polymer carriers with potential biomedical applications.

## Colloids for signal amplification in biosensing

Dr Robert Chapman

### Biography

Dr Chapman is a Lecturer in Chemistry in the School of Environmental and Life Sciences, and an adjunct lecturer in the School of Chemistry at UNSW. His research focusses on the use of high throughput polymerisation techniques to design polymer therapeutics. He has expertise in a broad range of polymer chemistry, peptide driven self-assembly, drug delivery, tissue engineering and in nanoparticle based biosensing. Prior to joining the University of Newcastle, Dr Chapman completed a BEng in Industrial Chemistry (2002-07) at UNSW. After a year working in management consulting for the Boston Consulting Group, he moved to the University of Sydney for his PhD in Chemistry (2009-12) under Profs. Sebatien Perrier and Katrina Jolliffe, where he studied the synthesis and self-assembly of cyclic peptide - polymer conjugates. From 2013-15 he worked as a research associate in the lab of Prof. Molly Stevens at Imperial College London on the development of nanomaterial based biosensors and scaffolds for tissue engineering. He then returned to the School of Chemistry at UNSW to begin his independent career as a Vice-Chancellors Research Fellow (2016) and DECRA fellow (2017-20), before moving to the University of Newcastle in 2020.

### Abstract

The ability to engineer and control structure on the nanoscale has enabled access to materials with extraordinary optical properties, which can interact with biological systems in unprecedented ways, and materials which are able to compartmentalise and release molecular components on demand. In this talk I will show how we have used liposomes, graphene dots and the plasmonic properties of gold nanoparticles to amplify signal for the highly sensitive detection of enzymes and proteins. The translation of these concepts into point of care devices for the diagnosis pancreatitis and rheumatoid arthritis by detection of very low levels of phospholipase A2 will be discussed.

## **Nature Nanotechnology**

Wenjie Sun

Associate Editor, Nature Nanotechnology.

### **Biography**

Wenjie joined Nature Nanotechnology in January 2017, following the completion of her PhD at ETH Zurich, Switzerland. She received her master's degree on colloid and interface chemistry and bachelor's degree on applied chemistry at Shandong University, China. During her PhD at ETH, she focused on the enzyme biochemistry and biophysics within soft matter systems. Wenjie is based in Shanghai.

### **Abstract**

Wenjie will talk about the scope of Nature Nanotechnology, the relationship of Nature Nanotechnology with Nature and other Nature Research journals. And she will share her experience on the editorial process (the workflow and the statistical data) and disclose the criteria of Nature journals from an insider's view. Through the talk, you will know better on what kind of papers a highly selective journal is looking for, how the editors decide whether to send a paper out or not, what they will do when the reviewers' comments are contradictory. And Wenjie is happy to share with you her personal experience as an editor if you are interested and what they are doing to increase fairness and transparency of publishing.

## **Newcastle – Oral Presentation Abstracts**

# Solid-electrolyte interphases in Aluminium-ion batteries

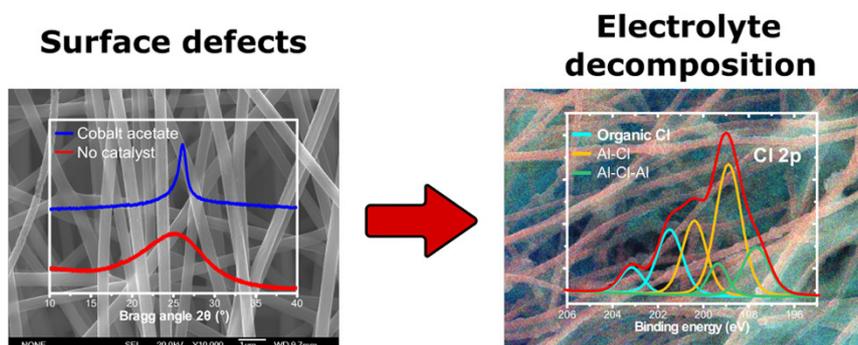
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The recent rise in the worldwide adoption of renewable energy vectors caused an increased demand for large-scale electrochemical energy storage. Current battery technologies such as lithium-ion, however, often lack the cost-effectiveness and safety requirements necessary for large-scale, grid-level energy storage applications. Therefore, it is important to search for alternative technologies, which are more suitable for this purpose. Non-aqueous aluminium-ion batteries (AIBs) are a promising emerging battery technology with several advantages over existing technologies and promising performance.<sup>1–3</sup>

Currently, one of the most recent challenges in this field involves understanding the phenomenon of poor coulombic efficiency in the first charge-discharge cycle, affecting some types of carbonaceous cathodes.<sup>4</sup> In this talk, we propose an explanation for this behaviour. By studying the performance of carbon nanofibres with varying degrees of graphitic character, the cause of the poor coulombic efficiency was found to be linked to the formation of a solid-electrolyte interphase, caused by the presence of surface defects in the carbonaceous cathode, promoting the premature decomposition of the electrolyte.<sup>5</sup>



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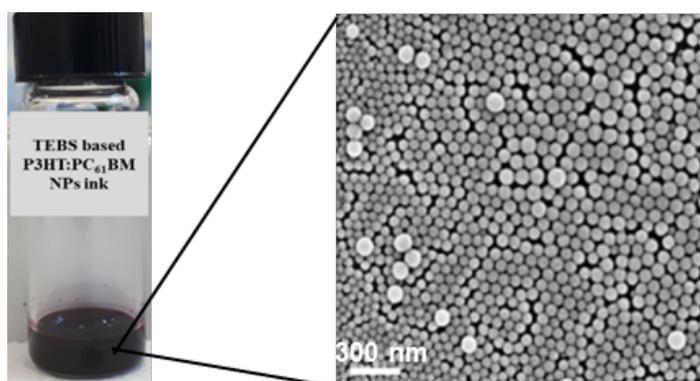
## Investigate the morphology of thiophene derivate 2-(3-thienyl) ethyloxybutylsulfonate sodium salt processed aqueous nanoparticles for organic solar cell application

Riku Chowdhury<sup>1</sup>, Natalie Holmes<sup>2</sup>, Warwick Belcher<sup>3</sup>, Paul Dastoor<sup>4</sup>, Xiaojing Zhou<sup>5</sup>

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An eco-friendly aqueous P3HT:PC<sub>61</sub>BM nanoparticles (NPs) ink has been synthesized using the water soluble thiophene derivate 2-(3-thienyl) ethyloxybutylsulfonate sodium salt (TEBS) surfactant for organic photovoltaic (OPV) device fabrication application. The internal morphology of the nanoparticles as well as their optical characteristics have been investigated using a combination of electron micrograph, UV-vis spectroscopy and x-ray diffraction (XRD) techniques. Most importantly, unlike the core-shell morphology of conventional sodium dodecyl sulphate (SDS) surfactant stabilized NPs, the TEBS NPs form an intermixed donor-acceptor nanodomains revealed by the scanning transmission x-ray microscopy (STXM) composition mapping. Furthermore, a systematic optimization study on TEBS processed NPs size and distribution explores a promising route of this green NPs for OPV (NP-OPV) device fabrication.



# Extended electrostatic decay lengths at very high salt concentrations: Examples and Implications

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Many colloidal properties are strongly dependent on the range and strength of Coulomb interactions. In the presence of other ions, the Coulomb interactions between ions are screened such that the interaction energy between charges is exponentially dependent on the separation, this is often expressed in terms of the Debye length.

The surprising observation of long-range electrostatic forces between surfaces immersed in ionic liquids and concentrated salt solutions<sup>1-5</sup>, has recently shown that at high electrolyte concentrations the electrostatic decay length is clearly *not* described by the Debye length and that the electrostatic decay length shows a minimum beyond which the range of electrostatic interactions *increases* with increasing electrolyte concentration.

Several examples of systems that exhibit long-range interactions at high salt concentrations will be presented and the implications discussed.

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# Understanding the assembly of amphiphilic additives in bulk and dispersed non-lamellar lipid-based matrices: Phosphorylation, H-bonding and ionisation

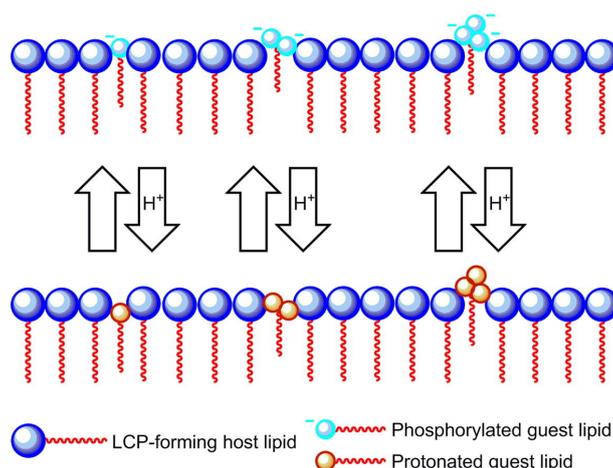
Wye-Khay Fong<sup>1,3</sup>, Marco F. Etter<sup>2</sup>, Alke Petri-Fink<sup>3</sup>, Barbara Rothen-Rutishauser<sup>3</sup>, Ehud M. Landau<sup>2</sup>

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The aqueous channel size of lipidic cubic phases can be a limiting factor for certain applications. For this reason, additives have been used to exquisitely control their nanostructure. In this study, two families of primary phosphoesters have been designed, synthesised and utilised to determine the effect of the positioning of the guest additive at the interface of the host mesophase, and to contrast the effect of headgroup ionisation and protonation.<sup>1</sup> A general methodology has been developed to produce primary phosphoesters, and a unique use of <sup>31</sup>P-NMR has been used in order to systematically investigate the influence of these additives on monoolein- and phytantriol-based bulk lipidic cubic phases and dispersed cubosomes.

In general, di-phosphorylated additives exhibit a greater effect upon lipid packing than the mono- and tri-phosphorylated molecules due to their optimal positioning (Fig. 1). In dispersion, the protonation state of the phosphate headgroups was manipulated by altering the pH, where shifts in pK<sub>a</sub> determined by <sup>31</sup>P NMR were used as a fluorescent label-free method to identify the location and ionisation state of the phosphate additives. This study systematically evaluates the influence of the positioning of the additive, headgroup size and charge of phosphorylated lipids on the behaviour of lipidic mesophases.



**Fig. 1** – schematic demonstrating how ionisation influences the positioning of mono-, di- and tri-phosphorylated lipids at the lipid-water interface in a lipidic cubic phase.

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## Extracellular vesicles: Don't hold you breath

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Research in the area of extracellular vesicles have exploded due to their novel biomedical applications, such as disease diagnosis or drug delivery. Extracellular vesicles are defined as nanosized particles with a lipid bilayer and are found in most bodily fluids. Their composition and physical properties are unique to the cell of origin, therefore extracellular vesicles can be used to determine whether a cell is diseased or not. Recently, the Goreham research group reported the isolation and characterisation of breath-derived extracellular vesicles.<sup>1</sup> Extracellular vesicles were isolated from breath condensate and subsequently captured onto a gold substrate using a self-assembled monolayer and an aptamer to target CD63 (a common target protein for extracellular vesicles). Electrochemical impedance spectroscopy measured an increase in resistance upon extracellular vesicle capture and this complimented the results obtained with surface plasmon resonance. This was the first report of the isolation, characterisation and capture of breath-derived extracellular vesicles and offers the first steps to a disease breathalyser.

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## Liquid marbles: Particle extraction and transport

Peter M. Ireland<sup>1</sup>, Benjamin T. Lobel<sup>1</sup>, Casey A. Thomas<sup>1,2</sup>, Syuji Fujii<sup>3</sup>, Grant B. Webber<sup>1</sup>, Erica J. Wanless<sup>1</sup>

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The electrostatic method of liquid marble formation allows contactless delivery of solid particles from a particle bed to a liquid droplet. This process has greatly expanded the variety of structures that can be formed, and the range of potential applications. To fully realise this potential, the process must be precisely controlled, and that requires a detailed understanding of the formation process. Three broad factors influence this process: (1) the morphology and strength of the electric field and the particles' reaction to it (2) the interparticle cohesion and friction forces in the particle bed and (3) the shape of the liquid droplet and the interaction of the particles with the liquid. Each of these three factors is coupled in a complex manner with the other two, and various approaches have been adopted to model them and their couplings. The electric field and electrostatic force on the particles were modelled analytically using an idealised sphere-charged plate model<sup>1,2</sup>, and more realistically using a finite element model realised in COMSOL Multiphysics. This latter model incorporated gravitational and electrostatic deformation of the droplet, and the resulting adjustment of the field morphology. Extraction of particles from the bed by the electrostatic force was modelled as a stochastic process analogous to the initiation of brittle fracture from micro-cracks<sup>3</sup>. One fascinating aspect of the interaction of non-conducting particles with the droplet was their mutually-distanced self-arrangement at the liquid/gas interface, possibly the result of lateral dielectrophoretic repulsion.

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## **‘Dumbbell’ polymer brushes: understanding the origins of non-monotonic structures**

Edwin Johnson<sup>1</sup>, Josh Willott<sup>2</sup>, Isaac Gresham<sup>3</sup>, Timothy Murdoch<sup>4</sup>, Ben Humphreys<sup>5</sup>, Stuart Prescott<sup>3</sup>, Andrew Nelson<sup>6</sup>, Wiebe de Vos<sup>2</sup>, Grant Webber<sup>1</sup>, Erica Wanless<sup>1</sup>

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Stimuli responsive polymer brushes offer the ability to modify interfacial properties such as wettability and lubricity as well as control biofouling. Surface-initiated ARGET ATRP has been utilised to synthesise pH and temperature responsive copolymer brushes which were subsequently characterised *in situ* with ellipsometry.<sup>1,2</sup> Neutron reflectometry (NR) revealed depletion regions in the polymer volume fraction profile (PVFP) near the silicon subphase resulting in ‘dumbbell’ like shaped PVFPs. There is no accepted mechanism through which depletion regions arise in brush conformations.<sup>3-5</sup> Numerical self-consistent field theory was employed to investigate the role segment configuration along the polymer chain has on the conformation of copolymer brushes. Enrichment of charge segments near the interface was found to be responsible for the increased brush hydration in the depletion regions. Understanding the origins of these unusual surface structures is important to develop relationships between surface structure and other interfacial properties.

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# Insight into Specific-Ion Effects in Aqueous, Non-Aqueous and Nanostructured Solvents from Quantum Chemical Simulations

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Specific-ion effects and the Hofmeister series have been known since the 1880s. Despite intense research, our understanding of their origins remains poor. We present multiscale quantum chemical simulations that probe how inorganic salts influence the structure and solvency of aqueous and non-aqueous molecular solvents. More complex nanostructured solvents, such as ionic liquids and deep eutectic solvents are also explored. These simulations provide new and fundamental insights into the origins of specific ion effects, for both aqueous and non-aqueous solvents [1,2]. On the basis of quantum chemical energy decomposition analyses, we propose a new mechanism for explaining reversals to the Hofmeister series based on the competing magnitudes of ion-solvent and ion-solute interactions, and their relative Lewis Strengths. We also report a new *ab initio* electrostatic descriptor that explains post-hoc observed specific-ion effects and Hofmeister series in a range of contexts, from polymer cosolvency, enzyme activity and the Gibbs Free Energy of transfer.

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# Liquid marbles using electrostatics: effect of particle conductivity, density and shape

Erica J. Wanless<sup>1</sup>, Benjamin T. Lobel<sup>1</sup>, Casey A. Thomas<sup>1,2</sup>, Syuji Fujii<sup>3</sup>, Peter M. Ireland<sup>1</sup>, Grant B. Webber<sup>1</sup>

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The electrostatic method for liquid marble formation has shown great promise in allowing contactless particle delivery to pendent liquid droplets. However, size has been shown to be a significant limitation in the selection of suitable particles for this transfer process. Here we reduce our previously reported size limitation<sup>1</sup> using conductive copper particles as small as 6  $\mu\text{m}$  diameter, delivering them to a 5  $\mu\text{L}$  pendent water droplet at applied voltages between 0.5 and 3.0 kV.<sup>2</sup>

The interplay of particle density, conductivity and cohesion have also been studied in relation to the successful formation of liquid marbles.<sup>3</sup> Here prior work on monodisperse, spherical latex particles has been expanded by adding thin conductive polymer shells to both these core particles and glass particles of similar size. Conductivity and cohesion have been shown to be competitive interactions with the former enabling and the latter hindering initial particle extraction from a negatively charged packed bed,. Whilst increasing the shell conductivity has previously been seen to facilitate particle extraction, this was not observed for the increased core particle density over the conductivity range studied. This was related to the increase in extraction force required to overcome gravitational forces with high-density particle samples found to more difficult to extract.

Conductive polymer coatings were also successfully applied to hexagonal polyethylene terephthalate platelets for subsequent study as liquid marble stabilisers.<sup>4</sup> The uncoated and coated platelets were used to form liquid marbles through both the traditional rolling and electrostatic transfer methods of water droplet encapsulation. Substantially different behaviour was observed compared to droplet stabilisation by spherical particles.

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## The structure of polymer brushes in complex environments

Grant Webber<sup>1</sup>, Edwin Johnson<sup>1</sup>, Hayden Robertson<sup>1</sup> Josh Willott<sup>2</sup>, Isaac Gresham<sup>3</sup>, Timothy Murdoch<sup>4</sup>, Ben Humphreys<sup>5</sup>, Wiebe de Vos<sup>2</sup>, Stuart Prescott<sup>3</sup>, Andrew Nelson<sup>6</sup>, Erica Wanless<sup>1</sup>

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Polymer brushes are routinely grown from solid substrates to change surface behaviour to suit particular applications. In many instances these properties, such as wettability, lubricity, adhesion and even anti-fouling, are related to the nanostructure of the brush. We have demonstrated brush structure can be finely tuned by varying solution pH, temperature or salt concentration and identity *independently*.<sup>1,2</sup> Here, a poly(ethylene glycol) methyl ether methacrylate (POEGMA) copolymer brush was exposed to aqueous solutions containing two electrolytes, where both salts were from the same end of the Hofmeister series or were from either end.<sup>3,4</sup> The net overall impact of electrolyte addition was found to be dependent on the relative amount of each salt and the system temperature. Copolymer brushes of poly(2-(2-methoxyethoxy) ethyl methacrylate) (PMEO<sub>2</sub>MA) and poly(2-(diethylamino)ethyl methacrylate) (PDEA) respond to changes in temperature and pH. When exposed to salt, the effect of each electrolyte on the copolymer brush conformation could be switched by changing the pH from low (charged DEA) to high (uncharged DEA).<sup>5,6</sup> The overall behaviour of the copolymer in each salt was PDEA-like at low pH, and MEO<sub>2</sub>MA-like at high pH.

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# Constructing monodisperse polymer micelles based on the concept of Platonic micelle

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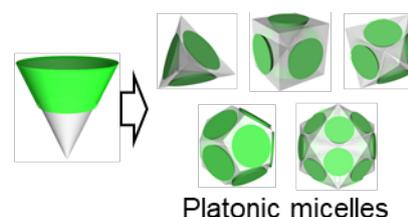
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It has been theoretically asserted and experimentally proven that the aggregation number ( $N_{agg}$ ) of spherical micelles is distributed over a range of values, so our knowledge of the thermodynamics of micelle formation suggests that truly monodisperse spherical micelles would not emerge. However, we previously demonstrated that when the  $N_{agg}$  of spherical micelles composed of calixarene-based amphiphiles is 20 or less, the structures are discretised and the  $N_{agg}$ s are always match the vertex numbers of regular polyhedra, that is, Platonic solids; therefore, these structures are named “Platonic micelles” (Figure 1).<sup>1</sup> We have so far identified many Platonic micelles in the micelle composed of small-molecular surfactants<sup>2</sup> and a reverse micellar system<sup>3</sup>. Therefore, we suppose that this concept of Platonic micelle is universal rule for any micellar systems, meaning it would also be applicable for constructing Platonic polymeric micelles.

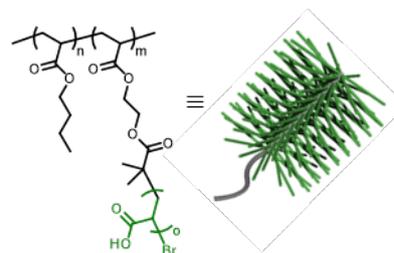
Controlling the interfacial area ( $a_e$ ) between hydrophilic domain and hydrophobic domain is required for constructing Platonic micelles. However, it seems to be difficult to control the  $a_e$  in the polymer system because of the flexibility of polymer chain conformation which is also affected by the solution condition such as pH, salt concentration, and temperature. In this paper, we employed molecular bottlebrush (MB) structure into the hydrophilic part to solve the problem. The  $a_e$  of the MB-based surfactant (MBS) can be systematically controlled using controlled radical polymerization. We evaluated the structure including the morphology and  $N_{agg}$  of MBS-based micelles using small angle X-ray scattering, light scattering, and analytical ultracentrifugation measurements, and will discuss it in the presentation.

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**Figure 1.** Schematic illustration of Platonic micelles composed of con-shaped surfactants.



**Figure 2.** Chemical structure and schematic illustration of molecular bottlebrush-based surfactant.

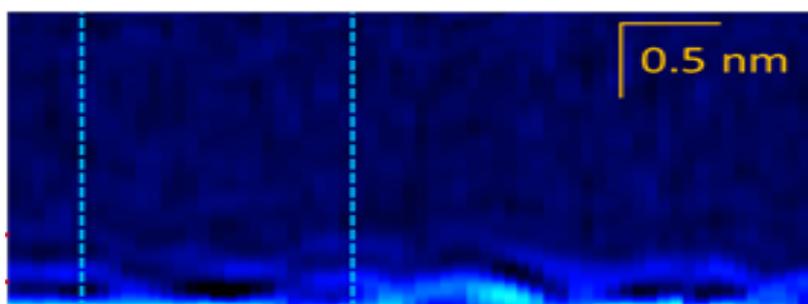
# Hydration Layer Structure of Biofouling Resistant Nanoparticles

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Hydrophilic surface chemistries can strongly bind water to produce surfaces that are highly resistant to protein adsorption and fouling. The interfacial bound water and its unique properties have intrigued researchers for decades yet the relationship between the water three-dimensional structure and function in antifouling coatings remains elusive. Here, we use hydrophilic, epoxy organosilane modified silica nanoparticles to demonstrate cheap, robust and practically applied coatings that we discover have broad-ranging, ultra-low antifouling properties when challenged by various proteins, bacteria and fungal spores. To understand their remarkable antifouling properties, Frequency Modulation-Atomic Force Microscopy is used to directly observe the interfacial water structure on single nanoparticles at sub-atomic resolution (Figure 1), which we validate using all-atom MD simulations that strikingly predict similar structures of water layers on the original and ultra-low fouling surfaces [1]. Unprecedented convergence of experimental and modelling data reveal that suitably spaced, flexible chains with hydrophilic groups interact with water molecules to produce a confluent, *quasi-stable* layer, consisting of dynamic interfacial water, provides an effective basis for antifouling performance of ultrathin, hydrophilic surface chemistries



**Figure 1:** 3D FM-AFM cross-sectional image of interfacial water structure on silica nanoparticle.

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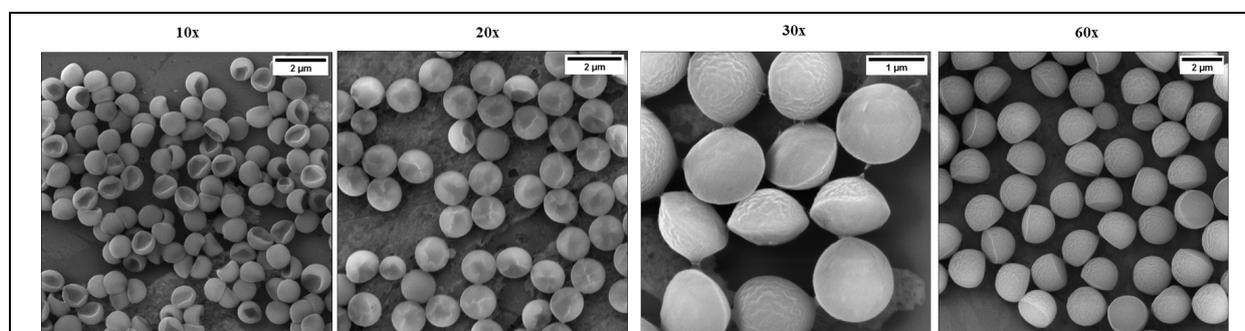
# A simple and flexible strategy for the preparation of non-spherical Janus particles

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The preparation of complex colloidal particles, *i.e.*, particles with non-spherical shape and asymmetric functionality, also known as Janus particles, has been the subject of numerous investigations in the literature. In spite of the broad variety of methods proposed over the last two decades, the preparation of Janus particles with controlled size, shape, functionality still remains a burden. The objective of this work is to propose a simple, reproducible and very flexible method to prepare polymer-based colloidal particles in the micron and sub-micron size range, with non-spherical shape and asymmetric functionalization. The method typically starts with simple polystyrene particles as seeds, and is followed by an activated swelling step with dioctanoyl peroxide, as both initiator and activated agent, a technique pioneered by Ugelstad three decades ago. This is followed by a second swelling step, where a variety of monomers (typically acrylates) can be used, and finally by free radical polymerization to consolidate the particles. This type of polymerization, leads to a Janus particles, with polystyrene confined on one part of the particle surface and the acrylates on the other side. When inhibitors are not removed during the second polymerization step, non-spherical particles are obtained, with shapes ranging from dimpled particles, to flattened spheres to diamond-like particles can be easily prepared, as shown in the figure, were particles prepared with different swelling ratios are showcased. In addition of being a highly reproducible synthesis, the particles are size controllable by playing with the seed size and the swelling ratio, easily functionalised by using functional acrylates, and can be easily prepared in very large quantities, making a unique example of how complex colloidal particles can be readily and flexibly synthesized.



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## Elasticity as a biomarker for cancer-derived extracellular vesicles

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Cancer cells can be up to 70% softer than their non-malignant counterparts and determining the cancer cell elasticity (how soft or hard a cell is) can be used as a cancer diagnosis tool. All cell types, including cancer cells, are known to release nano-sized vesicles, named extracellular vesicles (EVs), which can function as biomarkers for cancer. EVs are involved in cell-cell communication and are composed of DNA, RNA, and proteins within a phospholipid membrane that is specific to the cell they originate from. Although biomarkers in EVs offers a novel mode of cancer diagnosis, identification of biomarkers has been described as “finding a needle in a haystack”. With that said, there are bulk differences in the physical aspects of EVs such as the stiffness, size and adhesion properties. Atomic force microscopy of these lipid-based vesicles is a versatile technique that can be used to extract relevant physical information such as bending modulus of the lipid membranes, roughness of the surface of the vesicles, elasticity and adhesion. With this project, we aim to determine the elasticity variations between EVs derived from prostate cancer throughout the life-cycle (different degrees of metastasis). Preliminary results of this analysis are shown here with the relation of the different physical properties measured for normal prostate cell line-derived vesicles and the correlation of their adhesion, stiffness and deformation. This analysis will further be extended to probe EVs derived from prostate cancer cells of different metastatic potential. The results will further aid in cancer diagnostics and in improving the understanding of the active involvement of the EVs in cancer development.

## **Newcastle – Poster Abstracts**

# Discovery and Development of Drug Delivery Systems for Non-Ideal Active Pharmaceutical Ingredients

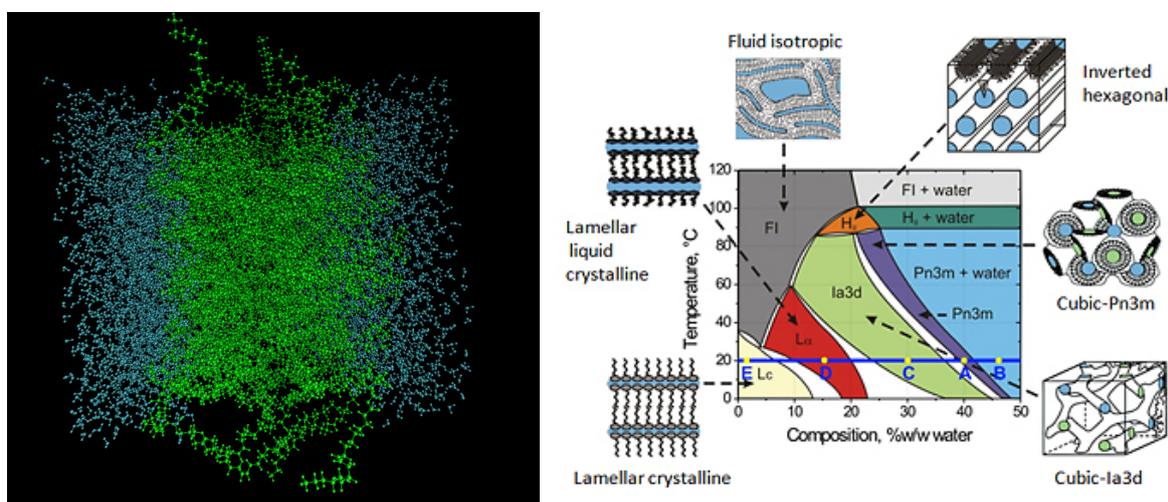
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Non-ideal active pharmaceutical ingredients (APIs) represent a significant share of existing pharmaceutical products as well as developing drug leads.<sup>1,2</sup> Both aqueous solubility and membrane permeability are properties crucial for drug efficacy *in vivo*, as they will affect the degree of drug transport and cell permeation.<sup>3</sup> One way to overcome the issue of poor aqueous solubility or membrane permeability amongst non-ideal APIs is the use of drug delivery systems; by encapsulating therapeutic cargo, the drug delivery system will supersede the properties of the drug with its own once in solution.

This PhD seeks to investigate drug interaction with potential drug delivery systems by complementing experimental and computational techniques, with the goal of using this information to discover and develop more effective drug delivery systems. Lipidic lyotropic liquid crystals (LLCs) and cucurbituril (CBn) inclusion complexes have been identified as potential candidates for development. Preliminary results of molecular dynamics simulations demonstrate spontaneous permeation of solubility limited Pitstop® 2 into a DOPC lipid bilayer (**Fig. 1**) when starting in the bulk water phase. By confirming simulations with experimental SAXS/SANS measurements, molecular dynamics can be utilized to give an atomistic resolution of drug position and kinetics in LLCs; something which is much more difficult to measure experimentally. Future work will involve modelling more complex LLCs (**Fig. 2**), as well as using density functional theory (DFT) calculations to assess the interaction of Pitstop® 2 with CBn macrocycles and potential analogues.



**Figure 1** (right) Molecular dynamics simulation of a DOPC bilayer  
**Figure 2** (left) Phase diagram of monoolein in water

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# Investigating the Interactions Between Lipidic Mesophases and the Human Gastrointestinal Microbiome

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This proposal aims to answer three clear questions about the interaction between the surface and internal structure of lipid mesophase particles that are inserted into the gastrointestinal tract, and the complexities of the human microbiome:

1. How does the lipid particle surface and structure influence the microbiome?
2. How does the microbiome influence the surface and structure of particles?
3. Can this mechanism be manipulated to enhance drug and nutrient absorption?

How drugs and nutrients are processed and absorbed by the body is still a poorly understood field of science, which limits the development of life-saving, cost-appropriate medications. This process is complicated by the action of the host's microbiome, which has been shown to metabolise both drugs and nutrients before absorption by the host.<sup>1,2</sup> Not only is microbial metabolism determined by the specific composition of the microbiota – which is highly variable across time and between individuals – but the drugs and metabolites present in this ecosystem also influence the composition of the microbiota.<sup>3,4</sup>

Lipid mesophases are promising matrices for drug delivery, offering significant benefits to existing oral formulations. Their biocompatibility, enhancement of drug stability and absorption, and stimuli-responsiveness have led to increasing interest in these nanomaterials. The encapsulation of enterally administered drugs in lipid mesophases is proposed as a method of mitigating complex drug-microbiota interactions. However, the fate of these nanomaterials in the gut is unknown, specifically, the role of the microbiota in this process.

Lipidic mesophases have shown to increase the absorption of actives on-demand, but their application has been limited due to an incomplete understanding of what happens *in vivo*.<sup>5</sup> In order to make advancements towards better nutrition and treatments, what occurs at the interface between these materials and the action of the microbiome needs to be understood.

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# Computational Investigations of Solvent and Ion Structure Containing Dissolved Ions at Varying Concentrations

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The presence of ions in many chemical, biological and physical systems can dramatically change the behaviour of that system<sup>1</sup>. A predictive theory of such effects is still elusive and much of this behaviour is ion-specific and not fully explained by a simple metric of the ion such as its size or charge, or by a property of the system such as concentration or dielectric constant<sup>2</sup>. These effects are known as specific ion effects (SIE), and a subset of this is the well-known Hofmeister series<sup>3-5</sup>. Observations of SIE are also not restricted to aqueous systems, and the understanding of ions in non-aqueous systems is much less understood<sup>3,6</sup>.

In this ongoing work, results from molecular dynamics (MD) calculations using the AMOEBA<sup>7</sup> polarisable force field are presented, examining how different concentrations of ions affect the structure of the solvent, and also how the ions themselves correlate with other ions. Concentrations ranging from 0.01-5m have been investigated, in an attempt to ascertain any discontinuities or irregularities as the solubility limit is approached, including re-entrant behaviour that is observed at high concentrations<sup>8-9</sup>.

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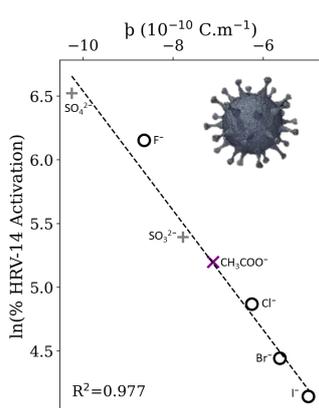
# The electrostatic origins of specific-ion effects

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Specific ion effects (SIEs) relevant to the physical, biological, chemical, environmental and material sciences have long gone without a fundamental understanding to their origins, or a subsequent predictive theory.<sup>1</sup> Existing theories are unable to adequately explain and predict frequently-observed series reversals and anomalies.<sup>2–5</sup> Building on previous work,<sup>6–7</sup> we establish the physical origin of the Hofmeister series of SIEs to be the dominant electrostatic potential energy ( $U_E$ ) of ions in the system. A new ion parameter,  $\rho$  (“sho”), correlates with SIEs in various water properties, co-nonsolvency effects and enzyme activities.  $U_E$  and  $\rho$  respectively provide the basis towards new general predictive theories and a tool for describing ion interactions.



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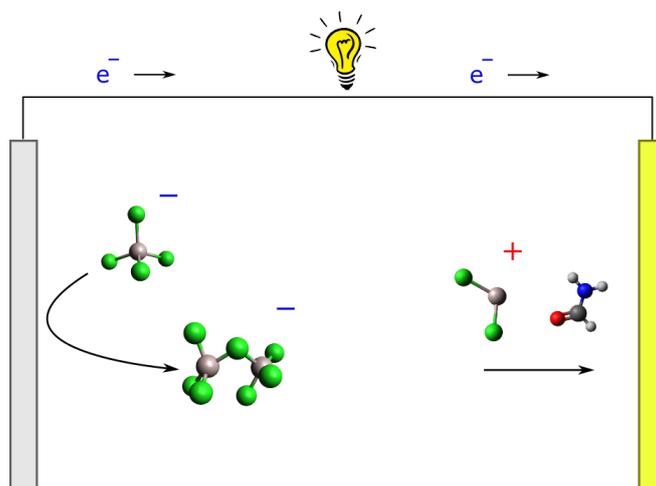
## Energy dense Al-ion batteries

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Aluminium batteries have the potential to provide a high capacity while offering greatly reduced costs in comparison to their lithium counterparts due to the over-whelming abundance of aluminium. However, current electrolytes are expensive and thus limit commercial viability. By using aluminium halide salts in a eutectic with a small polar compound, a cheap ionic liquid analogue can be obtained. These eutectic mixes have the added benefit of being less corrosive than the standard ionic liquids used. Herein we present some novel electrolytes with these cheap ionic liquids, as well as some conductive frameworks which provide capacity as well as delivering electrons into the other active material.



## Uniform Spacing of Particles on a Pendent Droplet Surface Under the Influence of a Non-Uniform Electric Field.

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During transport to a pendent droplet using an electric field in order to form liquid marbles<sup>1-2</sup>, certain hydrophobic particles have demonstrated a striking uniform spacing on the droplet surface during the initial stages of coating as revealed by video imaging at 180 fps (Figure 1). This phenomenon is exhibited by both conductive and insulating particles as long as they are sufficiently non-wetting. This work aims to elucidate the origin and factors that contribute to this significant interparticle spacing such as electric field strength, particle contact angle and particle conductivity.

To this end, insulating lycopodium spores were surface modified in order to vary particle contact angle. Whilst polypyrrole coated polystyrene of varying sizes (20 – 140  $\mu\text{m}$  diameter) were studied to investigate the impact of particle size on this unusual phenomenon.



**Figure 1.** 140  $\mu\text{m}$  hydrophobic conductive particles spacing out on a 5  $\mu\text{L}$  pendent droplet under the influence of a non-uniform electric field. Needle diameter is 1.2 mm for scale.

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# A novel pathogen sensing platform for detection of *Escherichia Coli* in Water

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Contamination of water by pathogens particularly *Escherichia Coli* (*E. coli*) presents a major challenge to human health today. These outbreaks not only burden healthcare systems but result in major financial and reputational damage to governments and water-treatment industries. The economic cost of managing impacts and plant shutdowns can be avoided by timely detection of the bacteria but most conventional techniques are labour intensive, time consuming and require high pathogen concentrations for effective detection. In this work, we capture and quantify outer membrane vesicles (OMVs) released by *E. coli* cells. As cellular excreta, these vesicles exhibit similar outer membrane proteins, composition and characteristics of the parent bacterial cell and can be used as abundant alternative targets<sup>1</sup> for *E. coli* detection. In doing so, we exploit specific DNA aptamers that selectively bind to the surface of OMVs, while examining their surface interactions and binding affinity to aid sensitive and efficient capture. In conjunction, we develop a dual detection platform that combines impedance based electrical and optical measurements to allow for rapid, robust and cost-effective detection of *E. coli* OMVs in potential industrial applications.



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## Specific ion effects on the behaviour of thermoresponsive polymer brushes

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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. One subset of specific ion effects is the Hofmeister series, which orders ions on their ability to either stabilise (salting-in ions) or destabilise (salting-out ions).<sup>1</sup> In recent years, thermoresponsive polymer brushes have been used as exemplar systems to study specific ion effects.<sup>2</sup> Thermoresponsive polymer brushes consist of end-grafted polymer chains, which undergo a phase transition from well to poorly solvated over a given temperature range, establishing an interface with switchable physicochemical properties.

The influence of mixed aqueous electrolytes and non-aqueous electrolytes on the behaviour of polymer brushes is limited, as there is no all-inclusive theory regarding specific ion effects. As natural environments are comprised of complex electrolytes, understanding the interplay of different ions in various solvents is imperative for real world applications. The thermoresponse of a poly(oligo(ethylene glycol) methacrylate) (POEGMA) statistical copolymer brush was monitored as a function of temperature in a variety of mixed electrolytes.<sup>3,4</sup> In the presence of these mixed electrolytes, a non-monotonic concentration-dependent influence of the two anions on the thermoresponse of the brush was observed. The manifestation of two salting-in ions on the behaviour of a POEGMA brush was dependent on the influence of the ions with the polymer chains, whereas the impact of two salting-out ions was dependent on the available solvent molecules. Much can be gained by improving our knowledge of ion specificity and understanding the subtle structural changes of a brush are essential to unravel the dominant drivers behind specific ion effects.

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## **Palmerston North**

9/2/21

## **Palmerston North – Keynote Abstracts**

## Emulsion Studies with Optical Tweezers

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### Abstract

This talk will describe two of the adventures we have had in our Optical Tweezers research, studying emulsion droplets.

1) Optical tweezers have been used to investigate the dependence of electrostatic inter-particle forces on separation, in systems consisting of pairs of either model silica beads or emulsion droplets. Measurements were carried out as a function of ionic strength and, at salt concentrations where the Debye length was larger than the standard deviation of Brownian fluctuations of the particles in the traps, results were found to agree reasonably well with the predictions of DLVO theory. Experiments were also carried out where the salt concentration of the environment was changed in real-time while interactions were continuously measured. Specifically, single pairs of particles or emulsion droplets were held in a microfluidic channel in close proximity to an interface created between milliQ water and a 5 mM NaCl solution. Changes in the force–separation curves were measured as a function of time and used to monitor changes in the Debye length, and thus the local salt concentration, as ions diffused away from the interface. The results were shown to be consistent with expectations based on a relevant diffusion equation.

2) The advent of technologies that allow the interactions of individual microscopic particles to be probed “one-at-a-time” has paved the way for new experimental avenues of enquiry in colloidal systems. However, while, for example, investigating a particular pair of colloidal particles isolated from a macroscopic sample might adhere together when brought into close proximity is certainly possible, it is currently still an arduous task to perform the experiment hundreds or thousands of times in order to acquire datasets worthy of confident analysis. We have constructed an automated particle collider for measuring particle-particle interactions by combining elements of microfluidics, holographic optical tweezers and image analysis. We envisage that such robust approaches to the automation of “one-at-a-time” experiments will find applications in a large number of areas, enable previously un-thinkable experiments to be carried out in a timely fashion, and allow the focus to shift away from tedious experimental frustrations to more profound scientific questions. As an example we measure variations in the sticking probability of pairs of emulsion drops with zeta potential.

## Biography



Bill Williams obtained an Honours degree in Physics with Astrophysics from Leeds University, UK and then undertook a PhD in NMR relaxation behaviour at the Open University. He went on to spend a number of years as a Postdoctoral Fellow in The Chemistry Department at York University, UK, working on various aspects of biological polymers. Subsequently he spent 4 years with Unilever Research, before returning to academia in March 2003, with a position in The Institute of Fundamental Sciences at Massey University, NZ, where he is working on biophysics and soft-matter.

## **Palmerston North – Oral Presentation Abstracts**

# WHEN LEGO BRICKS INSPIRE MICROSCOPIC MATERIALS: SUSTAINABLE PRODUCTION OF MULTIFUNCTIONAL PARTICLES

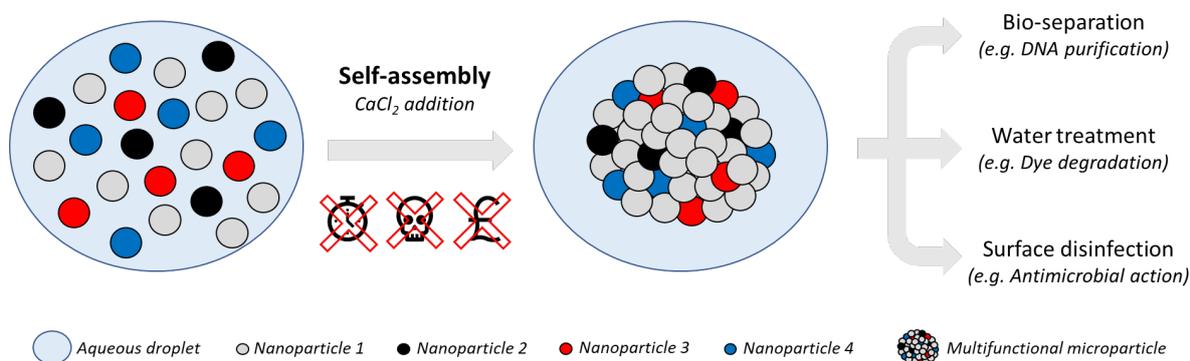
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Imagine reusable particles harvesting light to degrade organic pollutants from wastewater; magnetic particles able to extract and recover proteins of interest from solution or particles disinfecting surfaces before being recovered with a magnet. How many methods are needed to produce such systems? Based on current approaches, numerous, but what if the answer could be as simple as one?

We have designed a sustainable approach for producing multifunctional microparticles via salt-driven assembly of commercial nanoparticles dispersed in a water-in-oil emulsion.<sup>1,2</sup> In this method, the aqueous droplets act as a geometrical template controlling both the shape and size of the final particles. The use of nanoparticles as building blocks enables facile production of materials combining multiple properties, for instance magnetic, catalytic and adsorption. Using those two features, complex microstructures can be produced without the use of toxic chemicals, high temperatures, or bespoke lab equipment. The potential of this approach for real-life challenges is vast. Magnetic silica particles ( $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ) have recently been prepared for use in a low-cost biological separation technique for developing countries. Magnetic photocatalysts ( $\text{TiO}_2/\text{Fe}_3\text{O}_4/\text{SiO}_2$ ) have been produced as an easily recoverable system for adsorption and light-induced degradation of synthetic dyes from wastewater.<sup>2</sup> Antibacterial magnetic particles ( $\text{ZnO}/\text{CuO}/\text{Fe}_3\text{O}_4/\text{SiO}_2$ ) are currently being investigated as an inexpensive approach for disinfecting surfaces. All of these confirm our hypothesis that multifunctional microparticles can simply be *built up* in the same way as Lego.



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# Cytotoxicity of peptide self-assemblies of different structure, phase and reversibility towards neuronal and glial cells

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Functional amyloids have been found in a wide range of organisms, including humans, invertebrates and microorganisms. A decade ago, over 30 human peptide/protein hormones were shown to form functional amyloid aggregates inside the secretory granules of neurosecretory cells and exocrine cells<sup>1</sup>. Although interactions of disease-associated amyloids with biomolecules and cell membranes/model lipid membranes have been widely explored, limited literature is available on that of functional amyloids. In this context, we investigated the cytotoxicity profile of different types of molecular species formed during the neuropeptide self-assembly process, including soluble species and mature nanofibrils or nanotubes, either precipitates or as mesophases, towards two types of model brain cells, neuronal cells and glial cells. Three self-assembling human neuropeptides which were previously characterised by our group were used in this study<sup>2,3,4</sup>. Using a set of cell viability assays and biophysical techniques, we show concentration- and structure-dependent cytotoxicity of the neuropeptide self-assemblies. Peptide soluble species and liquid crystalline arrays of neuropeptide nanostructures are non-toxic. However, amorphous aggregates/precipitates formed at high neuropeptide concentration in cell culture media were correlated to cytotoxicity towards neuroblastoma cells and microglia. In contrast, amorphous aggregates formed by amyloidogenic peptides exhibited moderate cytotoxicity towards neuronal brain cell lines at all the concentrations studied. Our discovery will enhance the current understanding of functional amyloid toxicity and alarm the use of multicomponent solvent systems such as cell culture media to prepare the nanostructures for both fundamental and application research.

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# High Voltage Supercapacitors using microemulsion electrolytes

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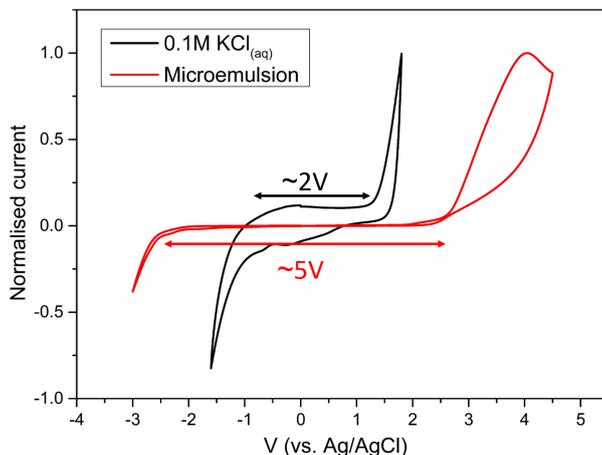
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In the diverse energy storage landscape, supercapacitors offer the advantage of fast charge and discharge making them ideal for high power applications such as accelerating vehicles or voltage stabilisation. The current standard electrolyte used in supercapacitors consists of an organic solvent (such as acetonitrile or propylene carbonate) and a quaternary ammonium salt. This combination has good electrochemical stability but is costly as well as potentially hazardous.

Using a water-based electrolyte is an attractive option, however, above a potential of 1.23V it is thermodynamically favourable for water to split into oxygen and hydrogen gasses. This means that under most circumstances aqueous supercapacitors are limited to around 1V at maximum. Traditional supercapacitors achieve voltages of between 2.7-3V, above which it is the electrode material (activated carbon) that begins to degrade rather than the electrolyte. This means that aqueous devices inherently have a lower energy density than organic devices.

I will present the first use of a microemulsion electrolyte, with water as the major component, in a supercapacitor with which we can achieve the standard voltage of 2.7 V. By breaking the 1.23 V barrier while remaining cheap and sustainable, we anticipate this electrolyte to have significant impact on aqueous electrochemical energy storage technologies. Commercialisation efforts are being actively undertaken and I will include aspects of this journey in my presentation.



## Slip-Induced Dynamics of Janus Spheres: Experiments

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In recent years, clusters of Janus particles have emerged as a new division of colloidal structures. Janus spheres have two distinct hemispheres<sup>1</sup> (Figure a), an asymmetry contributing towards interesting emergent structures when they aggregate. Our interest in the emergent properties of Janus spheres is driven by two factors. Firstly, there are untested simulation results suggesting that Janus particle clusters can form interesting phases.<sup>2</sup> Secondly, the asymmetry of Janus spheres suggests that the aggregation process could be controlled. One potential mechanism for controlling self-assembly involves the self-orientation of Janus spheres in flow. This is the subject of our current research relating to the dynamics of colloids with slip boundary conditions.<sup>1</sup> In preliminary experiments, free diffusion studies have been conducted to measure the diffusion coefficients of 600 nm and 800 nm diameter silica spheres. Control silica spheres were compared with hydrophobic (silane coated) silica spheres (see Figure b). Initial results indicate no detectable difference between the diffusivity of these beads, and further experimental studies are ongoing. The overall goal is to develop and study assemblies of asymmetric Janus spheres which have novel and/or interesting emergent properties, that is, macroscopic physical properties.

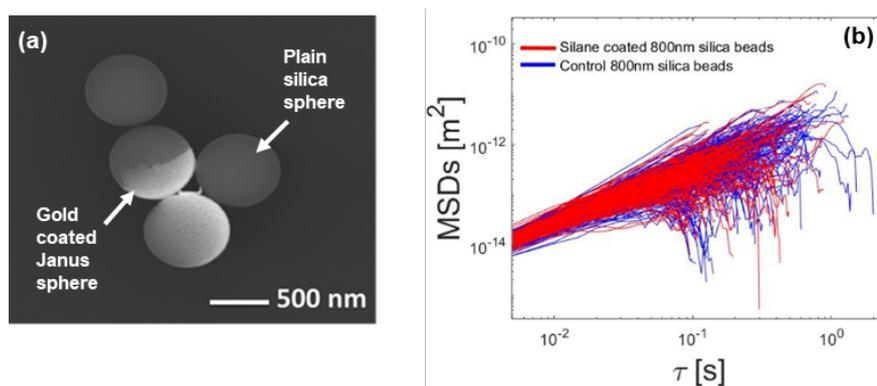


Figure: (a) SEM image of 800 nm gold coated silica Janus particles, and (b) mean square displacements (MSDs) as a function of time for diffusing 800 nm control and silane coated silica spheres.

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

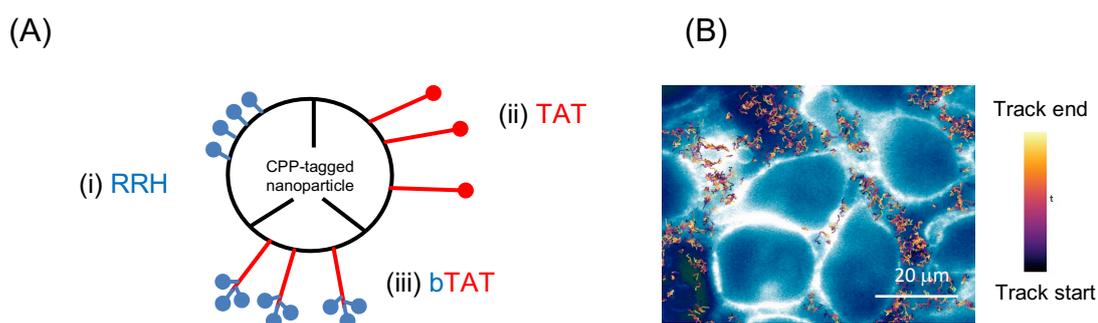
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Effective delivery of therapeutic compounds remains limited by our understanding of interactions between drug carriers at the nano-bio interface. Cationic cell penetrating peptides (CPPs) are reported to enhance the cellular absorption of therapeutic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

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



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

## Formation of fibrous aggregates of DNA and amphiphilic molecules at the air/water interface

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Although the interactions of nucleic acids with oppositely charged molecules have been studied for more than forty years, this subject still attracts great interest mainly due to the application of DNA/surfactant and DNA/polyelectrolyte complexes to the gene transfection into target cells. Although it is known that the layers of amphiphilic molecules at a liquid surface can be considered as physical models of biological membranes, and the information on DNA/surfactant interactions in the surface layer can facilitate the determination of the formation mechanism of the aggregates in biological systems, most of the authors considered the interactions of nucleic acids with surfactants and polyelectrolytes in bulk phases.

This work is devoted to the investigation of static and dynamic surface properties of mixed solutions of DNA with surfactants or hydrophobically modified polyelectrolytes, and to the estimation of the adsorption layer structure. Measurements of the kinetic dependencies of surface properties of the mixed solutions discovered a noticeable synergistic effect when the deviations from the results for solutions of individual components indicated the formation of a rigid network at the interface. The atomic force microscopy allowed estimation of the morphology of the adsorption layer as a function of the molar ratio of the two components.

### Acknowledgements

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# Molecular Dynamics Study of Janus Dimer Instability in Shear Flows

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Janus nanoparticles have received considerable interest recently due to the way that they interact with each other to self-assemble into complex nanostructures.<sup>1</sup> Theoretical studies suggest that these nanoparticles experience a torque in fluid flows due to their slip-asymmetric boundary conditions.<sup>2</sup> The torque on individual Janus nanoparticles promotes break-up of the aggregates into isolated spheres (see figure).<sup>3</sup> In this work, we investigate the effect of the hydrophobicity on the thermal- and shear break-up of amphiphilic Janus dimers. We will present our latest results on the possible break-up mechanisms and propose a descriptive equation for calculation of the break-up rate.

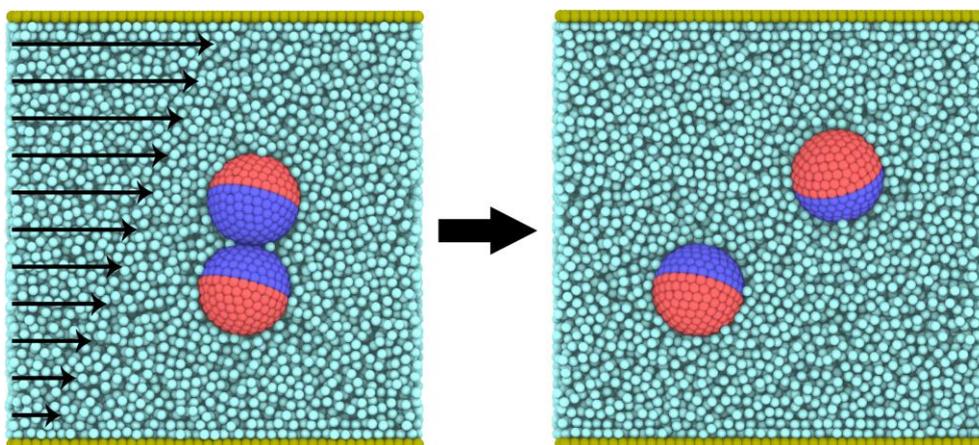


Figure: When an amphiphilic Janus dimer is in a shear flow, individual particles of the dimer encounter torque in opposite directions. This promotes break-up of the dimer into isolated spheres.

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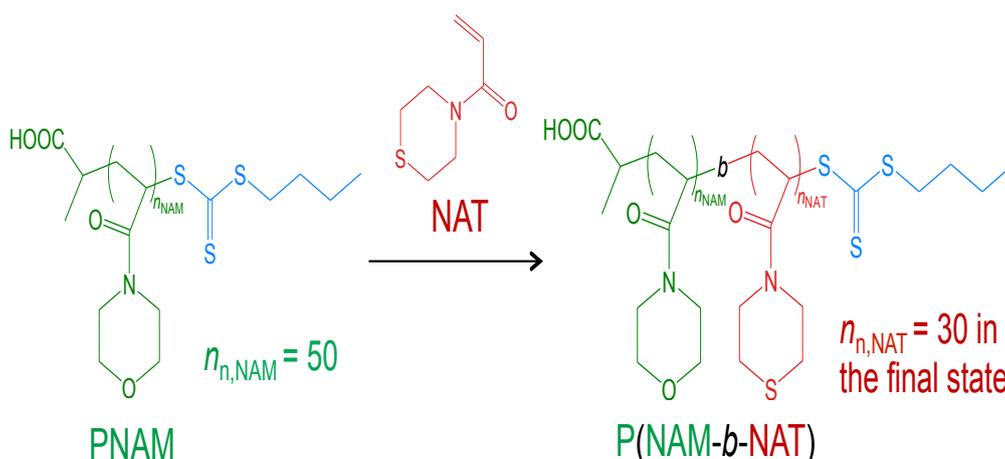
# A Kinetical Analysis of RAFT-Polymerization Induced Self-Assembly by Decoupling the Chain propagation and the Micelle Formation

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Upon extending a hydrophobic polymer chain from end of a preceding hydrophilic chain in aqueous solutions, the resultant block copolymers may eventually undergo self-assembly. Further chain propagation continues in the newly formed hydrophobic polymer rich domain. This process is often referred to as polymerization-induced self-assembly (PISA). Its kinetics are determined by the polymerization and the micelle formation/growth, which may influence each other. In this study, we examined PISA in aqueous solution on the reversible addition fragmentation chain transfer (RAFT) dispersion polymerization of poly(N-acryloylmorpholine)-*b*-poly(N-acryloylthiomorpholine). Using in situ small-angle X-ray scattering (SAXS) and nuclear magnetic resonance spectroscopy (NMR), the polymerization and micelle formation were observed. In the analysis, because the time scale of the micelle formation/growth is much shorter than that of the polymerization, the polymerization and micelle formation/growth can be decoupled. Thus, these were separately analysed in depth, and a combination of the kinetics of RAFT polymerization and the simple scaling theory of the micellar structures can quantitatively describe the overall micellar structural development during PISA.



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## Protein adsorption at the oil-water interface: role of protein self-association

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Many food emulsions are stabilised against drop flocculation and coalescence by thick films of adsorbed milk proteins at the drop surfaces.<sup>1</sup> The major protein in milk serum is  $\beta$ -lactoglobulin, a small globular protein. Depending on the pH, temperature, and salt concentration,  $\beta$ -lactoglobulin exists in aqueous solutions as monomers, dimers, or higher oligomers.<sup>2</sup>  $\beta$ -lactoglobulin diffuses rapidly from the aqueous phase to the oil-water interface. There it unfolds irreversibly to form a viscoelastic layer.<sup>3</sup> The surface charge of  $\beta$ -lactoglobulin and the hydrophobicity of the oil phase are known to affect the adsorption process.<sup>4-6</sup> In this talk, I will present results from a study done under conditions designed to tease out the differences in interfacial activity between the monomer and dimer species of  $\beta$ -lactoglobulin. We used drop profile tensiometry and interfacial shear rheology to probe the dynamics of the protein adsorption at the oil-water interface from aqueous salt solutions. We explored the influence of the salt concentration and the type of salt present on the elasticity of the protein network. Our key finding is that the formation of the viscoelastic layer is directly linked to the proportion of dimer present in solution. These results suggest simple routes for tailoring the properties of  $\beta$ -lactoglobulin networks at immiscible interfaces.

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## Ferrofluid Drop Impacts

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When placed in a magnetic field, drops of ferrofluid form spiky Rosensweig instabilities, so that their shape is often likened to that of a hedgehog. These fluids are suspensions of magnetic particles in a solvent, and instabilities arise from competition between surface tension and the tendency of the particles to line up along magnetic field lines.<sup>1</sup> The dynamics of these drops are not well-studied, and this presentation will discuss high-speed photography of vertical ferrofluid drop impacts on to a glass slide. A non-uniform magnetic field is present due to a bar magnet placed under the slide.

The form of the drop is of interest both before and after impact. Prior to reaching the surface, elongation of the drop (Figure, left) depends on the release height and the positioning of the magnet. Following impact, instabilities emerge on the spreading lamella and rim at various positions and times. When the magnet is close enough to the slide, the ferrofluid can be drawn radially outwards into a rim at the edge of the magnet (Figure, right).

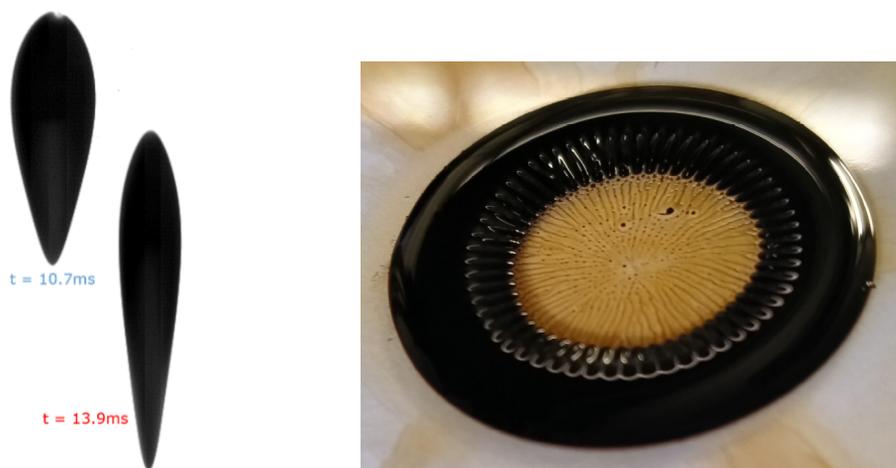


Figure: Left, ferrofluid drop profiles prior to drop impact on a glass slide placed above a bar magnet, labelled with relative time elapsed, and (right) a drop following impact.

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## **Palmerston North – Poster Abstracts**

## Diagnostic platform using Exhaled Breath Condensate

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Extracellular vesicles (EV) are tiny particles released by all mammalian cells and are found in bodily fluids, such as blood, plasma, serum and breast milk. The biogenesis of EVs leads to unique compositions that can be related to the parent cell (cell of origin) and can therefore be used in disease diagnosis. Various studies have shown that transmembrane and adhesion proteins present on EV membrane have the potential to serve as disease biomarkers. Our research group recently reported the isolation and characterisation of breath-derived extracellular vesicles for the first time.<sup>1</sup> This project builds on the previous findings to explore EVs as a non-invasive alternative for detection of lung-related problems. Breath-derived extracellular vesicles will be captured onto a gold substrate modified with a self-assembled monolayer and an aptamer to target specific ligands on the extracellular vesicle surface. Preliminary results show that electrical impedance is a reliable technique for measurement. Choice of thioic acid, period of immobilisation and surface preparation play vital roles influencing the electrode performance. Successful adaptation could provide a cheap, rapid and non-invasive diagnostic platform for lung-related problems.

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# Investigation into the application of light-manipulated Marangoni Flow in fluids

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Fluid motion typically is driven by a pump, mixer or other physical methods whereas biological systems often utilize the natural surplus of energy at interfaces to achieve flow. Recent developments in material science have shown the ability to achieve autonomous flow of fluid for almost no cost using the natural almost infinite surplus of energy at surfaces and interfaces, termed Marangoni flow.

This project investigated how to utilise this energy to drive droplet flow using phototaxis as already seen in literature, and the potential applications of such a system. Phototaxis of a droplet is achieved through the droplet containing a photoactive species and will be illustrated figure 1. Upon illumination of the droplet, the side illuminated will begin converting the photoactive species to a compound with different surface activity, causing a local surface tension gradient on the droplet. This gradient will cause a flow at the droplet interface which will transfer momentum to both the dispersed and continuous phase to drive droplet motion.

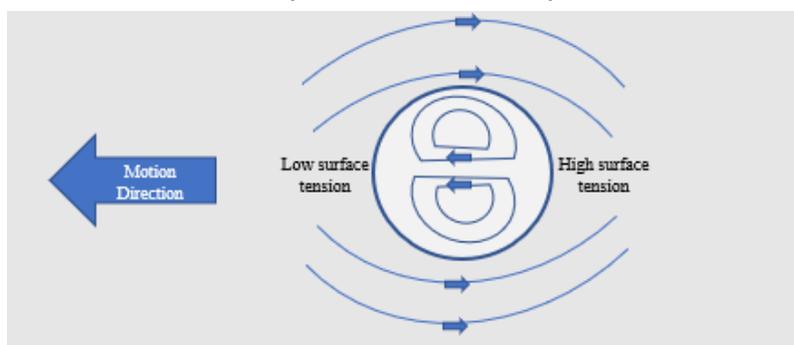


Figure 1: Schematic of droplet moving from Marangoni flow (based on schematic by Xiao et al. (2018))

The system investigated droplet motion and subsequent merge and polymerisation of two droplets, for potential additive manufacturing application. It was found that photo-induced polymerisation of two separate droplets was successful, but droplet motion did not occur with the given materials. These results showed the light wavelength (405nm)/photoactive compound (BAPO) combination could not provide enough energy to drive droplet motion and stresses the fact that such a system requires a strong combination to drive motion. This warrants further investigation into the system, including the use of a different photo-active compound and the use of a photosensitiser.

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## Hydrogen Sulfide Donor Particles

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In ischemic tissue, reperfusion leads to increase in reactive oxygen species (ROS) that can lead to further damage. Hydrogen sulfide (H<sub>2</sub>S) has been shown to help mitigate this damage<sup>1</sup>, therefore supplementation via polymeric particles could help reduce long term consequences of ischemic events<sup>2</sup>. Enhanced ROS levels can be used to trigger the generation of H<sub>2</sub>S from the polymeric particles allowing tissue specific release. The H<sub>2</sub>S was generated from the polymer itself; during degradation releasing a precursor that is enzymatically converted to H<sub>2</sub>S, bypassing low particle encapsulation of small molecules.

ARGET ATRP was used for polymer synthesis with a target MW of 11 kDa using a mPEG initiator and ascorbic acid as the reducing agent in a heterogenous solvent system. Hydrogen peroxide responsiveness was introduced via boronic ester pinacol groups on the monomers. Polymers were self-assembled using nanoprecipitation. Generation of hydrogen sulfide was measured via turn on fluorescence of 7-azido-4-methylcoumarin from polymeric particles when triggered via H<sub>2</sub>O<sub>2</sub>. Nanoreactors were formulated via loading of the particles with enzyme and removal of unencapsulated via centrifuge filters.

A series of polymers were synthesised that could generate H<sub>2</sub>S upon triggering with H<sub>2</sub>O<sub>2</sub> in the presence of enzyme. These polymers formed a heterogenous population of particles comprising of compound vesicles, vesicles and spongesomes, that upon exposure to H<sub>2</sub>O<sub>2</sub> cross-linked and formed stable particles. Exposure to H<sub>2</sub>O<sub>2</sub> also led to generation of H<sub>2</sub>S as detected via turn on of fluorescent probe. The presence of enzyme encapsulated within the particle allowed self-conversion of precursors to H<sub>2</sub>S. Enzyme did not escape from triggered particles yet small hydrophilic compounds did, suggesting the cross-linking allowed free exchange across the bilayer.

Polymers were synthesised that were able to generate H<sub>2</sub>S in environments of high oxidative stress, in response to H<sub>2</sub>O<sub>2</sub>. The cross linking of the particles allows encapsulation and retention of enzymes for self-conversion of the precursor to H<sub>2</sub>S. This opens for the potential use in ischemia reperfusion injury prevention.

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# **Sydney**

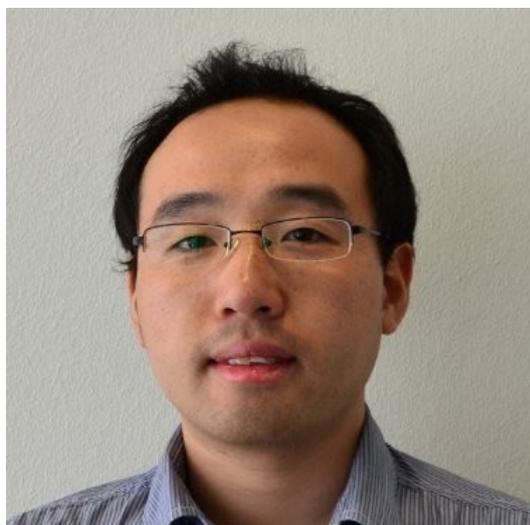
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## **Sydney – Keynote Abstracts**

## Multi-dimensional manipulation of Solid/Liquid interaction

Xu Deng, Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, China

### Biography



Dr. Xu Deng received his PhD in 2013 from the Max Planck Institute for Polymer Research. In 2014, Dr. Deng served as a postdoctoral fellow at UC Berkeley and Lawrence Berkeley National Laboratory. In 2015, he joined the University of Electronic Science and Technology of China as a professor. In 2017, He was pointed by the president of Max Planck Institute as the head of Max Planck Partner Group at UESTC. Dr. Deng is interested understanding of wetting dynamics, physical chemistry at interfaces. He has published more than 40 articles as first or corresponding author in leading journals such as Science, Nature, Nature Materials, Nature Communication, PRL, Angew Chem, Advanced Materials.

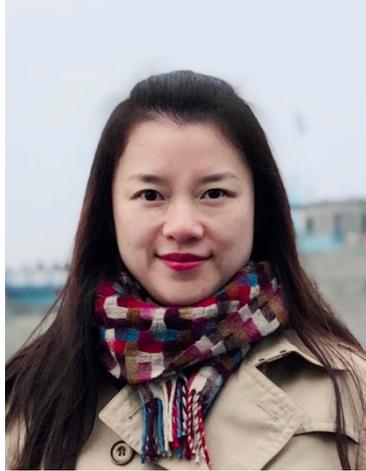
### Abstract

Solid/Liquid interaction play important role in many research and application fields. In this presentation, we will introduce a radically new strategy that resolves the bottleneck through the creation of an unexplored gradient in surface charge density (SCD)<sup>1</sup>. By leveraging on a facile droplet printing on superamphiphobic surfaces as well as the fundamental understanding of the mechanisms underpinning the creation of the preferential SCD, we demonstrate the self-propulsion of droplets with a record-high velocity over an ultra-long distance without the need for additional energy input. We envision that our work enriches and extends our capability in the manipulation of droplet transport and would find numerous potential applications otherwise impossible. We will also show that robust superhydrophobicity can be realized by structuring surfaces at two different length scales, with a nanostructure design to provide water repellency and a microstructure design to provide durability. The microstructure is an interconnected surface frame containing 'pockets' that house highly water-repellent and mechanically fragile nanostructures. This surface frame acts as 'armour', preventing the removal of the nanostructures by abrasants that are larger than the frame size. We apply this strategy to various substrates—including silicon, ceramic, metal and transparent glass—and show that the water repellency of the resulting superhydrophobic surfaces is preserved even after abrasion by sandpaper and by a sharp steel blade. This design strategy could also guide the development of other materials that need to retain effective self-cleaning, anti-fouling or heat-transfer abilities in harsh operating environments<sup>2</sup>.

## Protein sol-gel transition from liquid-liquid phase separation

Yi Shen, School of Chemical and Biomolecular Engineering, University of Sydney, NSW 2006, Australia

### Biography



Dr. Yi Shen joined the University of Sydney as a Lecturer in the School of Chemical and Biomolecular Engineering in September 2020. She aims to be an independent researcher in the field of protein biophysics, soft materials and microfluidics. Prior to this position, she was a postdoctoral research associate in the Chemistry Department, Centre for Misfolding Diseases at the University of Cambridge, where she was working on biophysical studies of protein liquid-liquid phase separation with Prof. Tuomas Knowles. She investigated the dynamics and probed the mechanical properties of biomolecular condensates by using microfluidic approaches. She completed her PhD in 2017 under the supervision of Prof. Raffaele Mezzenga in the Department of Health Sciences and Technology at ETH Zurich, Switzerland, where she developed novel organic-inorganic hybrid biomaterials based on protein fibrils and nanoparticles for food and nutritional purposes. Before her PhD, she also worked as a research staff with Prof. Howard Stone at Harvard University and Princeton University in the US, on bacteria/biofilm response to shear forces in microfluidic environments.

### Abstract

A range of biomolecules exist in the cell as liquid-like condensates and these condensates carry out essential biological functions in many systems, such as, signaling pathway, embryogenesis and RNA processing in their liquid state. It has been shown that a further liquid-to-solid transition (LST) of these condensates can lead to aberrant biology resulting cell malfunction. Thus, the kinetics and thermodynamics of protein phase behavior are at the heart of the onset and development of pathological protein aggregation. The previous studies have focused on the fundamentals of liquid-liquid phase separation (LLPS) of intrinsically disordered proteins in complex biological systems. However, the nucleation of pathological protein aggregates during the LST governed by physical factors remains unexplored. The present studies demonstrated that a range of biomolecular condensates can undergo a LST driven by shear force, forming beta-sheet rich nanofibrils<sup>1</sup>. Moreover, an approach combining microfluidics, infrared spectroscopy and advanced imaging was developed to map out the changes in the mechanical properties, secondary structures and thermodynamic stability of protein condensates undergoing the LST as a function of time. These studies explored the role of physical force in the protein aberrant aggregation and characterized the protein phase behavior from a biophysical point of view.

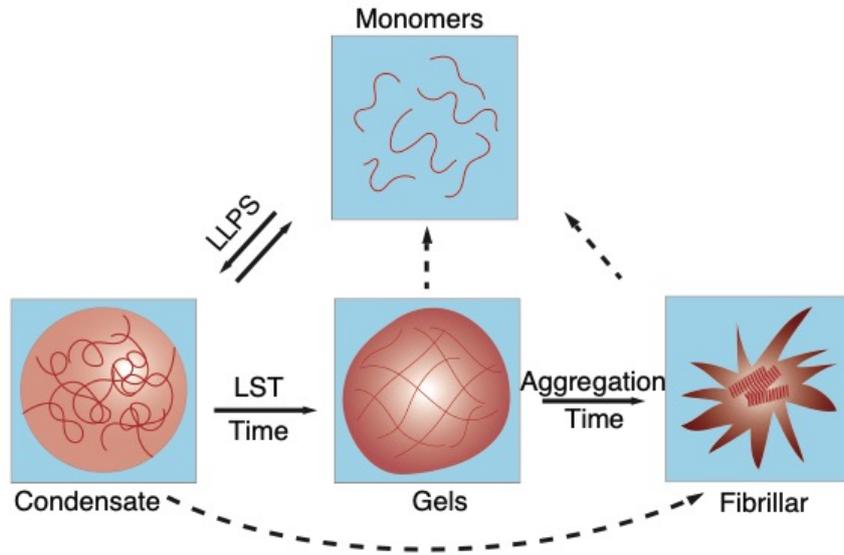


Figure 1: Protein phase transitions. Dispersed monomers can undergo LLPS to form condensates. The condensates can go further liquid to solid transition to form gels and fibrillar aggregates as a function of time.

## **Sydney – Oral Presentation Abstracts**

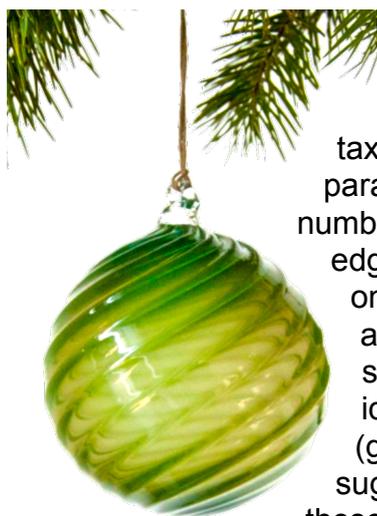
## (nano)Balls of (ssRNA) String

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Single-stranded RNA (ssRNA) folds onto itself in an extraordinary variety of forms, both *in vivo* and *in vitro*. Striking examples of ssRNA folds are the packaged RNA in viruses, from SARS (CoV-2)<sup>1</sup> to COVID-19<sup>2</sup>. We can think of folding as self-assembly of a one-dimensional string, due to various interactions between chemical groups within the string, including Watson-Crick complementarity (allowing substitution of Uracyl (U) for Thymine (T) in RNA), and between those groups and the solvent.



The 'simplest' assemblies - which can be very complex - are those containing double-helices and strand junctions only, induced by the sequence of base pairs along the string and Watson-Crick duplexing. I have developed a simple taxonomy of string duplexing, allowing for both parallel and anti-parallel helices<sup>3</sup>. The simplest fold families are those with an odd number of double-helices which wind around each of the  $(g+1)$  edges of 'lunar' nets in a strict order, forming anti-parallel helices on each edge of the net, forming genus  $(g)$  -2, -4, -6, folds. I argue (from a very naive theoretical perspective) that the ssRNA sequence can be designed to reproduce a theoretically idealised form, which is a symmetric ball-shaped cage, with  $(g+1)$ -fold rotational symmetry (point group  $C_{g+1}$ ). The idea suggests a number of interesting novel soft materials, where these RNA cages playing the role of (chiral, but with a spherical envelope) pseudo-particles.

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# Exploration of the limits of detection of microscopy Fourier transform infrared spectroscopy for the detection, quantification and identification of microplastics

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Microplastics are now widely acknowledged as a significant environmental pollutant, and can be found in soils, natural waters, biota and animals. Microplastics are typically considered to have a size range spanning five orders of magnitude, from the sub-micron to millimetre range. In order to fully understand the source, distribution, transport, fate and impact of microplastics in the environment it is necessary to be able to accurately physico-chemically characterise them. While the detection and characterisation of microplastics in the upper range of the size distribution is reasonably straight forward, as the size of the particles reduces, it becomes more challenging to characterise them appropriately. To do so accurately, it is essential to ensure that the testing instrumentation is fit-for-purpose for the sample under study and to understand the limitations of the technique being used for characterisation.

In this study, we aim to assess the limit of detection (LoD) of microscopy Fourier-transform infrared spectroscopy,  $\mu$ FTIR, in transmission and reflection mode using certified size standards of spherical polystyrene latex (PSL) particles. The approach described here can also be modified for a range of other commonly used techniques such as Raman spectroscopy, scanning electron microscopy or other methods.

Samples were prepared using PSL particles ranging from 2  $\mu\text{m}$  to 160  $\mu\text{m}$  diluted with ultrapure water and deposited on calcium fluoride slides for transmission mode or gold-plated reflective slides for reflectance mode. A  $\mu$ FTIR imaging system consisting of an Agilent Cary 620 FTIR microscope and an Agilent Cary 670 FTIR spectrometer was used for this study. For the instrument set-up used here, the LoD of the FTIR signal was established for single particles and clusters of particles.

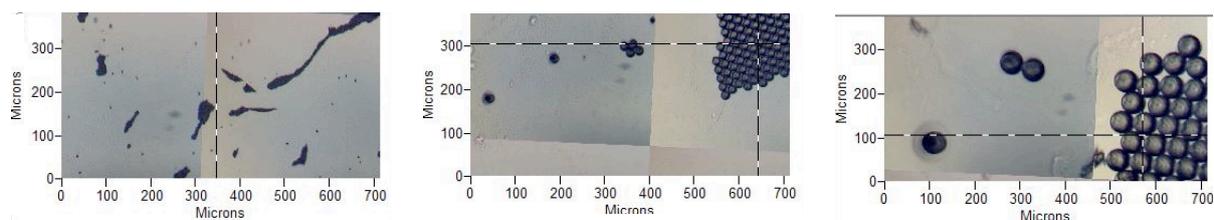


Figure 1.  $\mu$ FTIR images of 2  $\mu\text{m}$ , 10  $\mu\text{m}$  and 50  $\mu\text{m}$  PSL particles.

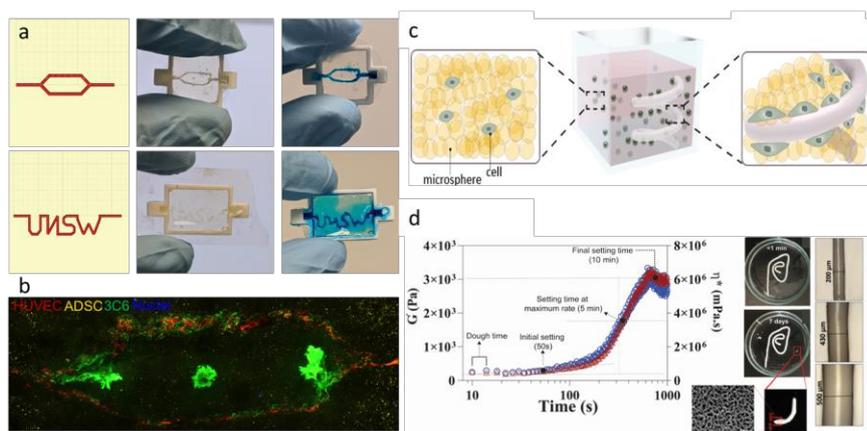
# Tailoring the mechanics and chemistry of yield stress fluids for bioassembly

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The extracellular matrix surrounding cells in tissue is a dynamic composite material, where the presentation of biophysical and biochemical information directs functional bioactivities. My laboratory is interested in how the properties of the extracellular matrix guides cell decision making and have developed a suite of engineered extracellular matrices to probe the biophysical and biochemical basis underlying cell programming and re-programming.



**Figure 1.** (a) Pluronics mediated printing within microgel suspensions. (b) endothelial lined (HUVEC) channels with adipose derived mesenchymal cells (ADSC) and melanoma microtumours (3C6). (c) Approach for printing ceramic inks into microgels with live cells. (d) mechanical characterisation of bone-ink setting.

Here I will show how geometric templating of tissue through a bioprinting approach within a cell-laden yield stress matrix of microgels can be used to direct cellular activity. First, I will demonstrate the direct writing of channels within the suspension using thermoresponsive pluronics (Figure 1a). Endothelial cells can be introduced in the void space to create prototype vessel structures. Printing tumour aggregates in proximity to the vessels provides a means to study cancer cell migration and intravasation. Next, I will demonstrate a novel calcium phosphate-based ink that rapidly precipitates into a nanostructured hydroxyapatite that shows mechanical properties of cortical bone tissue (Figure 1b). This sinterless technique allows complex bioceramic structures to be fabricated in the presence of live cells, with scope for translation to clinical settings. Finally, I will introduce a new approach for hydrogel engineering, where the mechanics and chemistry can be changed through applied force. These and other hydrogel-based model systems are changing the way in which fundamental biological questions can be probed, which will aid our understanding of biological processes while revealing new design parameters for regenerative biomaterials.

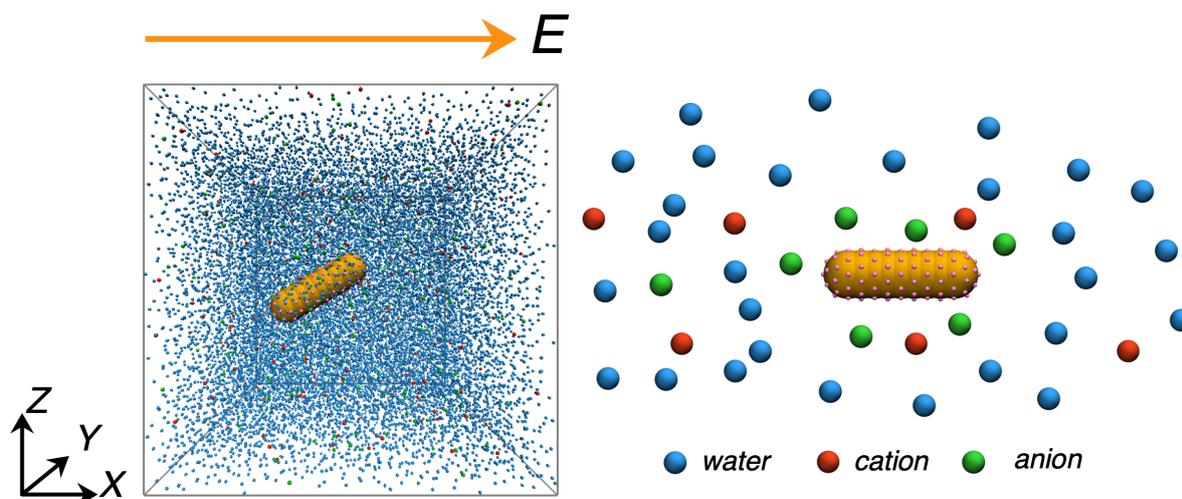
# Orientation of Gold Nanorods in Electrophoresis

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Our experimental collaborators demonstrate that the electrophoretic deposition (EPD) method can be used to assemble large arrays of vertically oriented nanorods with precise control of position at the single particle level on the patterned PMMA-ITO substrate. The orientation of gold nanorods during deposition is controlled by the electric dipole moment induced along the rod by the electric field. Using Dissipative particle dynamics simulations, we show that the magnitude of this dipole moment is dominated by the polarizability of the solution phase electric double layer around the nanorod.



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## **Nanoparticles and Surfactants: How they live, and how they dry**

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The drying mechanism of surfactant solutions and nanoparticle suspensions is important for their applications in coatings and paints, and is decidedly non-trivial. In addition to factors such as contact line pinning, surface tension, Marangoni forces, *etc.* that come into play for deposition, the changing concentration due to drying is complicated by the self-assembly of surfactant molecules into either micelles or liquid crystal phases.<sup>1</sup> This work aimed to examine how the formation of these self-assembled phases affects the drying process of systems containing both surfactant and nanoparticles.

Phases were designed with 0-60 % w/w dodecyltrimethylammonium bromide (DTAB, a cationic surfactant) and 0-5 % w/w 10 nm (diameter) silica nanoparticles. Larger concentrations effectively represented structures that were drier. Structural analysis was undertaken using small-angle neutron scattering (SANS), ultra-small-angle neutron scattering (USANS), and polarising light microscopy (PLM). Viscosity measurements were taken using a benchtop rheometer with a cone-and-plate set-up.

Silica nanoparticles were found to flocculate in these systems, though the size of these flocs decreased as the concentration of DTAB was increased. In turn, this decreased the opacity of the systems. Additionally, the viscosity of these systems increased as the concentration of either component was increased.

When droplets of silica solution were dried and examined using PLM, it was found that silica particles dried into large structures in the centre of the droplet. When DTAB was present, the far more birefringent surfactant crystals were found beyond the silica structures, and were also apparently incorporated into the silica structure. At higher concentrations of DTAB, the silica structures were disrupted, likely as a consequence of the smaller flocs in solution. This caused a more homogeneous drying process compared to the samples with silica, but with a decreased birefringence compared to a silica-free system. This latter effect was likely because the smaller silica flocculates could act as defects in the wider surfactant crystal structure, weakening the long-range order and birefringence.

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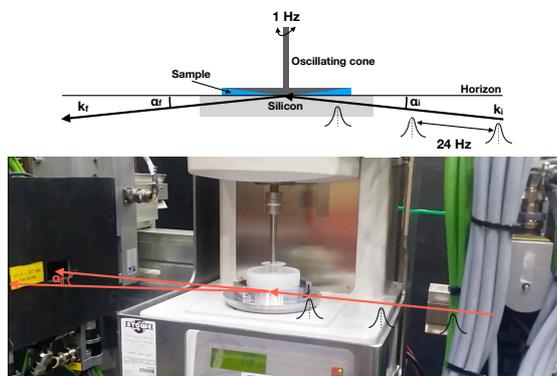
# Time resolved in-situ grazing incidence scattering from a surfactant/magnetic nanoparticle composite under oscillatory shear

Andrew Nelson<sup>1</sup>, Apurve Saini<sup>2</sup>, David Simone<sup>2</sup>, Franz Adlmann<sup>2</sup>, Maximilian Wolff<sup>2</sup>

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The horizontal sample plane of the *PLATYPUS* neutron reflectometer permits in-situ rheology measurements using the cone and plate geometry of a rheometer. *PLATYPUS* is normally used for determining surface normal interfacial structures, but it can also be used for examining in-plane lateral structure using Grazing Incidence Small-Angle Scattering. Historically the majority of these type of in-situ experiments have studied steady state conditions (“what happens to my adsorbed layers at different shear rates?”). It is relatively straightforward to perform such equilibrium measurements, but significantly more difficult to examine time-dependent processes; mainly because neutron scattering is signal limited and neutron instrumentation was not developed enough. *PLATYPUS* was specifically designed to study kinetic processes. It acquires data in event-mode (every scattered neutron is recorded), which allows both single shot, and stroboscopic, measurements to be performed. Stroboscopic measurements apply a period impulse to a sample, with counting statistics built up over many cycles. Recently we developed the capability of recording event-mode information from the sample, in a parallel stream to the neutron events, allowing timescales of  $\sim 40$  ms to be probed. Here we leveraged this world-leading capability to study a concentrated F127 mesophase with magnetic nanoparticles dispersed in the interstitial holes, with a view to developing magnetically tuneable properties of a surfactant crystal [1]. The system was studied under oscillatory shear, with NR and GISANS scattering patterns being obtained from each point of the sinusoidal strain/velocity curve. The intensity of the  $\langle 111 \rangle$  peak (=degree of ordering) of the FCC micellar crystal depends on the shear rate, with the signal being maximised at lowest shear rates.



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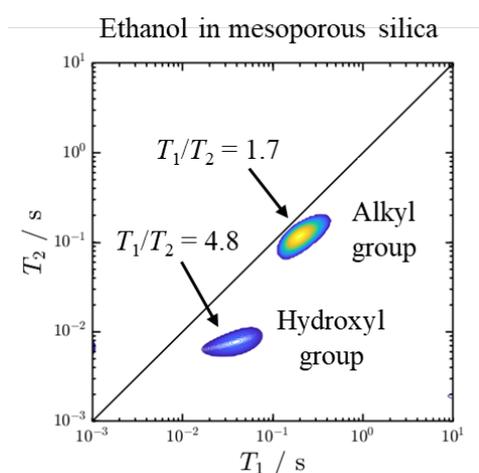
# NMR relaxometry: a non-invasive probe of surface phenomena in porous media

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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 and separations. NMR 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. In particular, the use of 2D correlation data allows the clear comparison relaxation phenomena exhibited by liquid mixtures, or by different chemical groups, such as the alkyl and hydroxyl proton behaviours of adsorbed alcohols (see image below). 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,<sup>1</sup> and as a potential method for fingerprinting adsorbate interactions at the pore surface.



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# Structural and Double Layer Forces between Silica Surfaces in Suspensions of Negatively Charged Nanoparticles

Liam R. J. Scarratt, Katarzyna Kubiak, Plinio Maroni, Gregor Trefalt, Michal Borkovec

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Concentrated suspensions of charged nanoparticles are relevant in numerous applications, such as papermaking, ceramic processing, and food technology. One of their unique properties is the liquid-like structuring of nanoparticles, which has been shown to originate from the double layer repulsion between them. This property has been heavily explored in the last 10 years, predominately by colloidal probe atomic force microscopy (AFM) using like charged confining surfaces (Fig. 1a).<sup>1</sup> Here, the resulting force profiles show an oscillatory behaviour with wavelengths of several nanometres (Fig. 1b) as nanoparticle layers are squeezed out. However, despite the wealth of knowledge of these oscillatory structural forces, less information is available on the double layer forces acting in these systems at confining surfaces which dominate at smaller separations resulting in a particle-free layer. Here, we present direct force measurements between negatively charged silica microparticles carried out in suspensions of like-charged nanoparticles with colloidal probe AFM. At smaller distances, soft and strongly repulsive forces are present due to double layer repulsion between the like-charged surfaces, which is quantitatively interpreted with the Poisson–Boltzmann (PB) model adapted to a strongly asymmetric electrolyte to capture the nonexponential nature of these forces. By modelling the nanoparticles as highly charged co-ions, while the counter ions are monovalent, this model permits extraction of the effective charge of the nanoparticles and helps further understanding of the particle-free layer at confining surfaces.<sup>2</sup>

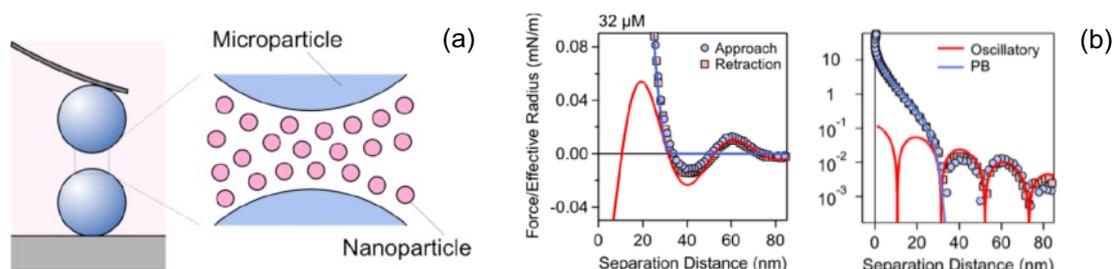


Figure 1. (a) Schematic of a commonly used colloidal probe AFM experiment for probing nanoparticle structuring. (b) Resulting force vs separation profiles in linear and semi-log representation with nanoparticle concentration given in  $\mu\text{M}$ .

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# Modulating the properties of biocompatible materials via microfluidic thermophoretic transport to control cellular activity

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Most of the biggest challenges in tissue engineering rely on the capability to adjust and manipulate a variety of different materials building blocks at the micro- or nano-scale to control cell-substrate and cell-cell interactions. Here I demonstrate an innovative approach to locally control the mechanical properties of gellan gum hydrogel based on the manipulation of molecules, polymers and particles exploiting thermophoresis (i.e. the gradient of concentration induced by the presence of a temperature gradient)<sup>1</sup>. This was achieved by fabricating Joule heaters in-situ within a microfluidic device and by flowing cold water to create a transverse temperature gradient<sup>2</sup> to induce a concentration gradient in the solution before crosslink (see Fig. 1a). After extrusion, the rigidity of the material was characterised by Atomic Force Microscopy whereas its porosity was investigated by Scanning Electron Microscopy (see Fig. 1b,c). This method permitted, for the first time, to control the mechanical properties of the substrates on the micron scale independent of the chemistry.

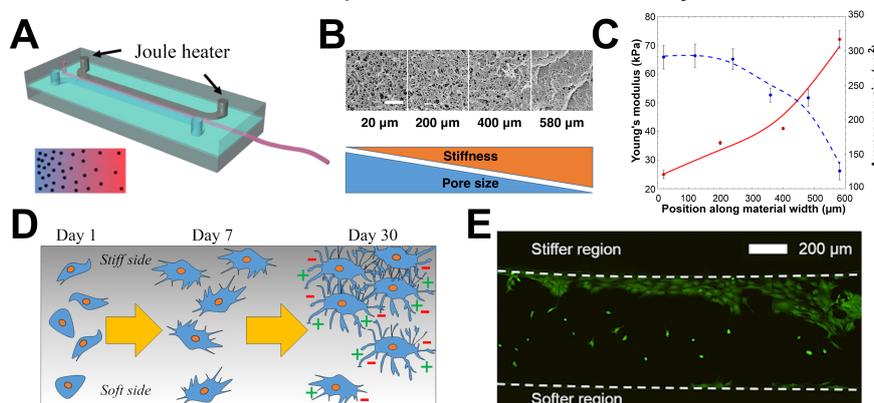


Figure 1: A – Schematic of the device and principle of thermophoresis; B – SEM images captured across the material width (scale bar = 500 nm); C – pore size (blue symbols) and stiffness distribution (red symbols) along the material; D – Schematic representation of osteoblasts activity on the substrate over time. After 30 days a mineralization gradient is observable (the red “-” signify  $\text{PO}_4^{3-}$  and the green “+”  $\text{Ca}^{2+}$ ); E – live/dead assay confocal image of the cell distribution after 7 days over the gradient material.

The mechanical cues embedded in the scaffold were then used to guide the migration of MC3T3 osteoblasts (i.e., bone cells) and to control their capability to mineralise the substrate (see Fig. 1d,e). These cells showed a preferential migration and proliferation towards the stiffer side where they also produced higher mineralization. These results establish a new route to controlling the microstructure of cell culture matrices.

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## The Tribology of Hair and its Control

Deborah Wakeham<sup>1</sup>, Andrew Greaves<sup>2</sup>, Colette Cazeneuve<sup>2</sup>, Nawel Baghdadli<sup>2</sup>, Roberto Santoprete<sup>2</sup>, Mark W. Rutland<sup>3,4</sup>, Gustavo S. Luengo<sup>2</sup>

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Fibre – fibre interactions play an important role in hair movement, look and feel. Besides the physical structure of the hair fibres, the chemical composition of hair creates a variety of interaction forces between neighbouring fibres which affect the adhesion and friction as the hairs slide past one another. The ability to control these interactions through the use of hair-styling products to achieve the desired hair movement (or lack thereof), as well as texture, is of great interest.

In this study we first examine the frictional and adhesive forces between two hair fibres in ambient conditions before and after applying a strong polyelectrolyte, poly-diallyldimethylammonium chloride (polyDADMAC), based conditioning treatment. Three hair samples were analysed: natural hair, chemically bleached hair, and chemically permed hair. The results showed a strong hair type dependence on the friction coefficient as well as directional and angle sliding effects, attributed to hair surface roughness, cuticle lifting and cuticle – cuticle interlocking. A difference in the response of the various hair types to the conditioning treatment was also observed, including a significantly different adhesion mechanism between the fibres.

We will also present the results of the behaviour of two natural hairs grafted with 3-mercaptopropionic acid and 11-amino-1-undecane thiol molecules. These molecules were specifically chosen to modulate the forces acting between the surfaces according to pH. The results show that it is possible to reversibly switch the interactions, and their magnitude, between an attractive and repulsive state by changing the pH conditions.

# Fatty acid vesicles experience multiple barriers to fusion

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Phospholipid bilayers are central to living organisms. However, prior to the existence of phospholipid-based cell membranes, it is likely that primitive cells on Earth were made of simpler molecules that had a single acyl chain rather than the two acyl chains of phospholipids.

One model system explored for primitive cell studies are fatty acid vesicles. Rather than self-assembling into micelles, fatty acids are able to self-assemble into bilayer membranes at a pH near the apparent  $pK_a$  and encapsulate material (Fig. 1).

In this presentation we explore how to attain full fusion between fatty acid vesicles. We use a recently reported method to generate solutions of giant fatty acid vesicles.<sup>1</sup> We find that in addition to being extremely colloidally stable, owing to the high surface charge density of the membranes, the dynamic nature of the membranes can counterintuitively also limit full fusion. We will then discuss strategies for further fusion studies.

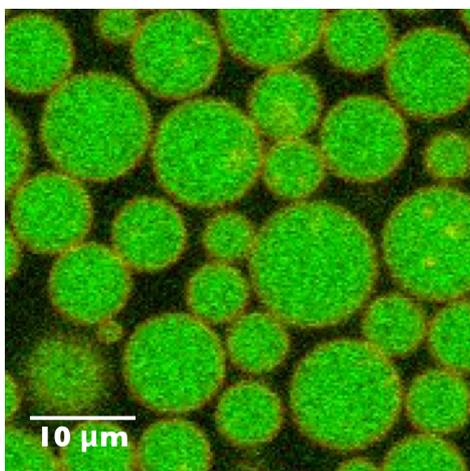


Figure 1. Confocal microscopy image of oleic acid vesicles encapsulating 1 mM pyranine (green).

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# Flexibility of Lipid Bilayer Membranes in Ionic Liquids

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Ionic liquids (ILs) are a novel class of solvents with ultra-low vapour pressures and tunable liquid properties. Among them, protic ionic liquids (PILs) are particularly effective solvents for self-assembly of surfactants and lipids into micelles, vesicles, liquid crystals, and microemulsions.[1-4] This is exemplified by alkylammonium PILs, which are also cheap, easily-prepared and can be readily deuterated. Over the past decade, much has been learnt about the static structure of many PILs,[5] however, little is known about their dynamics, or how the underlying nanostructure of the IL solvent affects the dynamics of amphiphile aggregates. In this work, we examine the effect of solvent nanostructure on flexibility of lipid bilayers. We employed neutron spin echo spectroscopy (IN15, ILL) to probe the mesoscopic undulation of egg-PC vesicle bilayer membranes in ethylammonium formate (EAF), ethanolammonium formate (EtAF), and their water mixtures. For the first time, IN15 is configured to perform dynamic measurements up to 1000 ns, which is essential due to the much slower motion we observed in PILs. By comparing these ILs with water, we are able to elucidate the dominant factor that affects membrane stiffness and stability in ILs, and how IL nanostructure contributes to the dynamics of large amphiphile aggregates.

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## Material Thrombosis at Interfaces

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Blood-contacting medical devices can cause potentially fatal blood clots (thrombosis) unless patients receive systemic blood thinning, anti-thrombotic drugs. However, anti-thrombotic drugs can themselves lead to severe bleeding complications. In order to combat these issues, multidisciplinary researchers have been working to develop anti-thrombogenic materials and surface coatings. Despite over 50 years of research in this area, the community is yet to develop a truly non-thrombogenic material or coating. While there are many potential causes, our failure is partly attributed to the complex nature of thrombus formation at material interfaces and our remaining limited understanding of the interplay between the material, biological and dynamic (blood flow) factors involved<sup>1</sup>.

Material thrombosis is driven by protein adhesion (causing the enzymatic coagulation cascade to polymerise fibrinogen into the biopolymer fibrin) and cell adhesion and activation (platelets and leukocytes). We have developed a range of *in vitro* systems to understand thrombus formation on a range of materials and under both static and dynamic blood flow conditions to investigate different aspects of material thrombosis. Under static conditions, we characterized the fibrin thrombus structure on materials with increasing wettabilities and found that decreasing wettability correlates with decreased fibrin fibre density at the interface. We additionally developed a novel microfluidic system to visualize fibrin and platelet accumulation in real-time on a range of materials under increasing shear rates using whole human blood. We demonstrate material, shear rate and anticoagulant dependent fibrin polymerization patterns and platelet aggregation patterns.

These findings provide insights into thrombosis at material interfaces and these systems will allow further evaluation of a variety of materials under physiological and pathological blood flow shear rates to better understand medical device-induced thrombosis.

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## **Sydney – Poster Abstracts**

# Structured polymer coatings by self-assembly approach and their application in atmospheric water capture

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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. The fundamental of PDRC material is to minimise energy gain from incident solar radiation ( $\lambda = 0.3 - 2.5 \mu\text{m}$ ) and maximise radiative heat loss transmitting through the atmospheric window ( $\lambda = 8 - 13 \mu\text{m}$ ). Among various established designs of PDRC, diffusive light scattering based on refractive indices difference is a popular way to achieve desired solar reflectivity. Herein, we prepared a hierarchically porous polymer film from poly(vinylidene fluoride-co-hexafluoropropylene) through a controlled evaporation phase inversion technique. The film morphology is greatly dependent on experimental variables during formation including environmental condition, polymer-solvent interaction, applicational thickness, additives, etc. We characterised the hierarchically porous structure (SEM, SANS, USANS, MICP, etc.), the film surface wettability, and assessed the cooling performance by custom built apparatus. Eventually, the films were integrated within a prototype for passive atmospheric water harvesting, demonstrating promising avenues of future research.

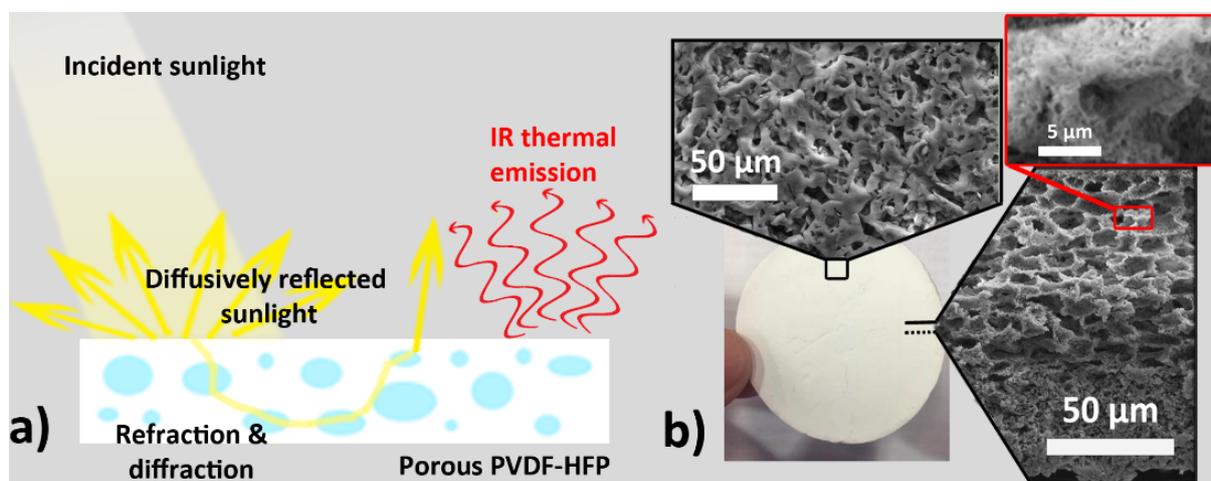


Figure 1. a) Schematic representation of the passive cooling fundamentals. b) SEM images showing the hierarchically porous structure on surface and cross section.

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# Kookaburra, the ultra-small-angle neutron scattering Instrument at ANSTO: RECENT APPLICATIONS

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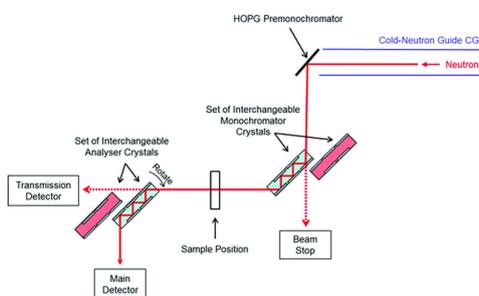
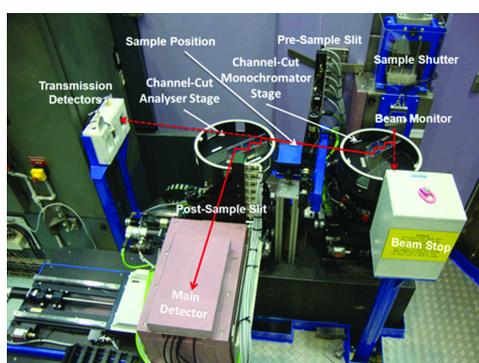


Figure 1: The layout of the KOOKABURRA USANS instrument at ANSTO with the main components indicated.

The double-crystal ultra-small-angle neutron scattering (USANS) diffractometer Kookaburra at ANSTO was made available for user experiments in 2014. Kookaburra allows the characterization of microstructures covering length scales in the range of 0.1–10  $\mu\text{m}$ . Use of the first- and second-order reflections coming off a doubly curved highly oriented mosaic pyrolytic graphite pre-monochromator at a fixed Bragg angle, in conjunction with two interchangeable pairs of Si(111) and Si(311) quintuple-reflection channel-cut crystals, permits operation of the instrument at two individual wavelengths, 4.74 and 2.37  $\text{\AA}$  (Figure 1).

This unique feature among reactor-based USANS instruments allows optimal accommodation of a broad range of samples, both weakly and strongly scattering, in one sample setup [1,2]. The versatility and capabilities of KOOKABURRA have already resulted in a number of research papers, including studies on hard matter systems like rocks and coal [3,4], as well as soft matter systems like hydrogels or milk [5,6]. This clearly demonstrates that this instrument has a major impact in the field of large-scale structure determination. Some of the recent examples will be presented here.

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# Dynamic Multilayered Hydrogels for Modelling Cancer Invasion

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The tissue microenvironment is an orchestra of heterogeneous populations of multiple cell types continuously reorganizing their surrounding matrix over time, and disruption of this homeostasis can lead to disease. Impairments in extra cellular matrix (ECM) such as matrix stiffening or softening, changes in composition and structure, and improper degradation or formation of ECM can lead to fibrosis and cancer<sup>1–3</sup>. Additionally, cell-cell and cell-matrix interactions affect cell morphogenetic processes<sup>4</sup>, e.g., in the epithelial to mesenchymal transition (EMT), cuboidal closely packed epithelial cells see a decrease in E-cadherin expression which causes them to lose cell affinity and cell polarity causing it to transition into migratory loosely packed mesenchymal stem cells which expresses more of N-cadherin<sup>5</sup>. Mimicking much of this complexity *in vitro* has proved to be a considerable challenge.

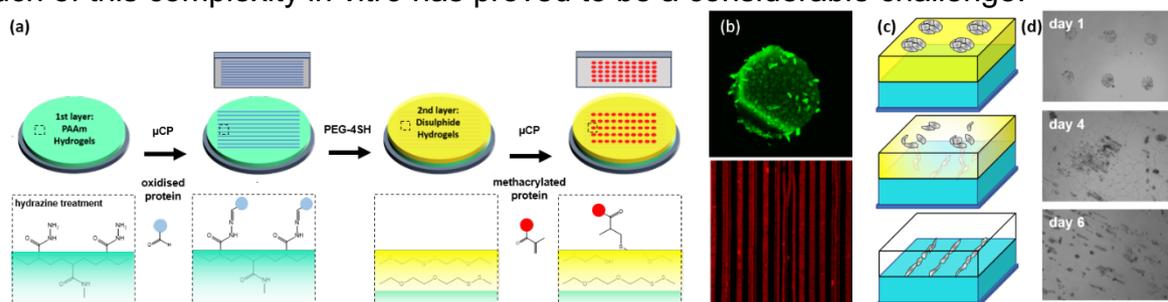


Figure 1. (a) Schematic of fabrication of multilayered hydrogels followed by protein micropatterning. (b) Representative laser scanning confocal microscope images of disulphide hydrogels (circle) when patterned arylate fibrinogen fluorescein and PAAm (grid line) when patterned oxidised fibrinogen fluorescein. (c) Schematic of cells degrading disulphide gels and repatterning (d) Brightfield images of cell degrading disulphide gels over day 1 to day 6

Herein, we present a simple approach to fabricate multilayered hydrogels system consisting of cell secreted enzyme degradable hydrogels of tuneable stiffnesses and chemistries. We also present a novel technique to pattern hydrogels with cell adhesion proteins using compression and soft lithography as confirmed by fluorescence microscopy. Cells adhere to these compressed regions in accordance with underlying matrix proteins as a function of stiffness. We demonstrate how closely packed tumour cells in circular patterns secrete enzymes over time, thereby degrading the first layer of disulphide gels, and subsequently re-pattern onto the second polyacrylamide hydrogel. This dynamic multilayered hydrogel system may prove useful in emulating changes in shape observed during morphogenetic processes as commonly seen when tumour cells transition from an epithelial to a mesenchymal state during invasion.

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## Development of a novel microfluidic platform to study material thrombosis under flow

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Blood-contacting medical devices are commonly used in modern medicine, these devices can differ greatly in design and complexity e.g. catheters, artificial heart valves, left ventricular assist devices (LVAD). A common cause of medical device related complications is the development of blood clots (thrombosis) at the blood-material interface, this can result in fatal complications such as device failure or clot emboli causing stroke. When blood contacts a foreign material, thrombosis is thought to be initiated by protein adsorption and subsequent conformational changes leading to protein activation and activation of the thrombotic pathways<sup>1</sup>.

The contribution of material surface properties, blood components, and variations in flow conditions to thrombosis is complex and interdependent. Many *in vitro* models of biomaterial thrombosis focus on individual aspects of the system, however, the interplay between material surface properties and variations in flow conditions is poorly understood in biomaterial thrombosis<sup>1</sup>.

We developed a microfluidic model to study blood-biomaterial interactions under various flow conditions as verified with finite element analysis software (ANSYS Fluent). To fabricate our devices, we utilised photolithography to produce a master mould in photoresist (SU8-2100) and cast with polydimethylsiloxane (PDMS). Devices were reversibly bonded to the material of interest and perfused with whole human blood. Platelet adhesion and fibrin formation were observed in real time using fluorescence microscopy on a variety of materials subject to a range of flow rate and anticoagulant combinations. This model enables the investigation of thrombotic failure mechanisms on existing medical device materials under dynamic flow conditions and may serve as a platform to screen newly developed surface coatings to reduce thrombosis.

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## Organisation of a solvent mixture near a nanoparticle

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Inorganic nanoparticle cores are often coated with organic ligands to control their growth and solution stability in apolar solvents. However, the structure of the ligand shell depends strongly on the core size, temperature and solvent quality.<sup>1-3</sup> In particular, ligand ordering can rapidly change the interaction between nanoparticles in dispersion from repulsive to attractive, causing the particles to agglomerate.<sup>2</sup> In addition, the temperature at which the particles agglomerate has been shown to increase with increasing solvent chain length due to preferential stabilisation of the ordered ligand state.<sup>3</sup> Since solvent mixtures are often used to tune the dispersibility of nanoparticles for different applications, it is important to understand how the ligands behave in such mixtures.

In this work, we investigate what happens when the ligand coated nanoparticles are immersed in a mixture of two apolar solvents with different chain length. We characterise how the solvent mixture organizes around the nanoparticles and how the ordering temperature of the ligands depends on the composition of the mixture. In particular, molecular dynamics simulations were used to study hexadecanethiol passivated gold nanoparticles in a binary mixture of hexane and hexadecane solvent. Our results show that the solvent preference near the ligand shell strongly depends on how ordered the ligands are. In the ordered state, the ligand shell is preferentially solvated by the hexadecane molecules, whereas hexane molecules preferentially solvate the ligands when they are in the disordered state. Remarkably, the ordering temperature of the ligands still increases linearly with the fraction of hexadecane atoms in the mixture. This occurs because there is no solvent preference near the ligand shell at the midpoint of the ordering transition, which means that the ligands see a well-mixed solvent at that point, despite the clear separation at higher and lower temperatures. Further work is underway to determine if this behaviour changes as the solvents become less similar.

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# Protein-Driven Coagulation of Blood on Liquid-Infused Surfaces

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Thrombosis (blood clot) induced by blood-contacting medical devices can cause potential complications in clinical settings through device failure, stroke and mortality. It is well established that the adsorption of prothrombotic proteins in the blood such as Factor XII (FXII) and fibrinogen instigate the cascade of events which ultimately lead to material-thrombosis.<sup>1</sup> In the intrinsic pathway of coagulation, activation of factor XII (FXIIa) is of particular importance and has been shown extensively to form preferentially on hydrophilic, negatively charged materials and is associated with faster coagulation in the context of biomaterials-induced thrombosis.

Liquid-infused surfaces (LIS), have recently been shown to decrease material thrombosis and biofilm formation.<sup>2</sup> This is achieved by immobilising a liquid layer on a surface coating to create a slippery interface that prevents the adhesion of blood components and bacteria.<sup>2</sup> However, in order to successfully translate these functional materials, an understanding of the mechanisms responsible for their low thrombogenicity is necessary.

In this work, we characterise a type of LIS, the tethered-liquid perfluorocarbon (TLP). We investigate the activation of the intrinsic coagulation pathway in the presence of TLP materials, showing that the TLP surfaces result in minimal FXII activation and clotting compared to a hydrophilic surface. However, coagulation following the intrinsic pathway was not found to be vastly different compared to a surface that is hydrophobic. We probe the possible mechanisms by which the anti-thrombotic TLP surfaces function and potentially, for liquid-infused surfaces in general, through the concept of enhanced protein and cellular mobility at the blood-TLP interface.

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## **Magnetic nanocomposite hydrogels for directing myofibroblast activity in adipose derived stem cells**

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Dynamic cell culture materials that can change mechanical properties in response to extrinsic stimuli are emerging as promising tools for cell and tissue engineering research. However, most of these techniques involve one-way stiffening or softening and do not afford reversibility. Here we demonstrate the incorporation of superparamagnetic iron oxide nanoparticles within poly(ethylene glycol) hydrogels as dynamic cell culture materials. Using simple permanent magnets and adipose derived stem cells, we see a near 2-fold increase in cell spread area and an accompanying 20% enrichment in cells expressing alpha-smooth muscle actin. This platform provides a means to study relationships between dynamic stiffening and cell behaviour, using permanent magnets and clinically viable composite materials, with scope for use as a tool to enrich the myofibroblast population in stromal cells.



# Optimising atmospheric water capture: a study into the dynamics of water nucleation and roll-off

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Atmospheric water capture is a promising avenue to supplement existing sources of clean water, and it relies on the nucleation and collection of dew droplets on a cold surface.<sup>1-2</sup> It is well known that nucleation of water is easier on high surface energy substrates due to lower energy barrier to nucleation,<sup>3</sup> but the exact quantification of this effect has not been performed as a function of different surface chemistries and controlled surface roughness. In this work we did two sets of experiments: on the one hand we quantified the number of nucleation sites versus wettability (surface energy) and droplet population before coalescence. On the other hand, we quantified the critical radius of droplets for detachment, and map nucleation sites (whether droplets repeatedly nucleate on the same spot) as a function of surface energy and heterogeneity of the tested surfaces. The environmental chamber built for the latter experiments (Figure 1) allows us to study these properties under tightly controlled conditions of temperature differential and humidity.

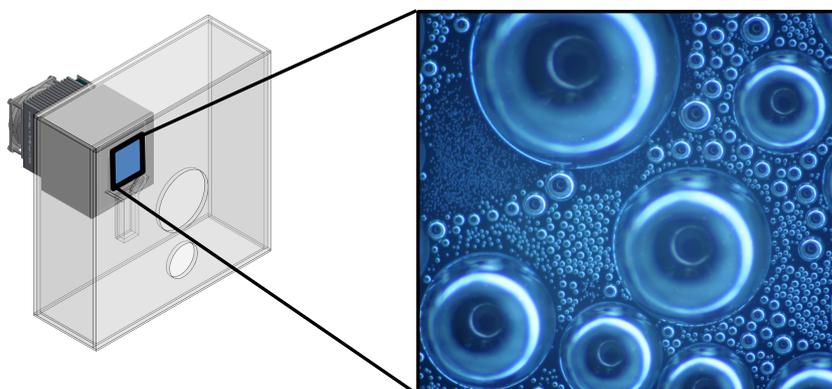


Figure 1. Apparatus developed to investigate water condensation dynamics under humidity and temperature control.

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# Emulsion stabilization mechanism by whey protein-sodium alginate complex

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Emulsion stabilization using protein-polysaccharide complex is a common method to facilitate various emulsion-based food formulations including beverages, powder, gel and edible films. Dairy proteins, due to their amphiphilic nature, tend to be adsorbed and display viscoelastic properties at the interface, enabling a crucial role as natural food emulsifiers<sup>1</sup>. Addition of polysaccharide in dairy protein-stabilized emulsions can further improve emulsion stability for nutraceutical encapsulation. Studies have demonstrated that emulsion preparation techniques can influence the physical properties of emulsions stabilized by protein-polysaccharide complex and control the structure of the interfacial layer<sup>2-3</sup>. This presentation addresses the stabilization mechanism(s) in emulsions produced by soluble whey protein-sodium alginate complexes based on their preparation routes and polysaccharide concentration. Whey protein and a corresponding anionic polysaccharide, sodium alginate, were chosen to observe the impact of polysaccharide addition to the protein-stabilized emulsion. The current understanding on biopolymer behaviours as a function of pH and the main interactions in complex formation will be presented. Emulsion characterization including macroscopic and microscopic observations, turbidity, zeta-potential, droplet size, creaming index and rheological measurements will be critically analysed to evaluate the overall emulsion properties and stability during storage in a comprehensive manner. The outcomes would provide useful insight into designing food grade biopolymer complex carrier for encapsulation purposes.

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## Emu cold-neutron backscattering spectrometer at ACNS, ANSTO

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Emu is the high-resolution neutron spectrometer installed at the OPAL reactor, ANSTO, which delivers 1  $\mu\text{eV}$  FWHM energy transfer resolution for an accessible  $\pm 31 \mu\text{eV}$  energy transfer range.<sup>1</sup> The spectral resolution is achieved by neutron backscattering from Si (111) on the primary and secondary flight paths, allowing up to 1.95  $\text{\AA}^{-1}$  momentum transfer range. The spectrometer is well suited for quasi-elastic and inelastic neutron scattering studies, notably in the field of soft-condensed matter, like lipids, gel and colloids including biophysics and polymer science, chemistry and materials science.

Most experiments are carried out with standard cryo-furnaces (2 to 800 K temperature range). Spectrometer beam-time access is merit-based, thus welcoming as well experiments in other materials research areas, and including experiments that may require e.g. other ancillary equipment such as existing controlled-gas delivery, and potentially pressure, applied field set-ups, etc. Examples of the spectrometer capabilities are shown through select case studies.

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# Image analysis for z-axis AFM calibration at the sub-nanometre level based on a new secondary realisation of SI metre

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The resolution achievable in the vertical (z-axis) with atomic force microscopy (AFM) is one of its fundamental advantages as an imaging and characterisation instrument for nanoscience. Translating this resolution into measurement accuracy typically requires a careful calibration with appropriate transfer artefacts featuring step heights traceable to a realisation of the definition of the SI metre. To date, the step heights of commercially available, fabricated artefacts have been limited to no smaller than approximately 10 nm. This compromises the accuracy at the sub-nanometre level required for metrology tasks such as measuring the thickness of two-dimensional materials and characterising the surface roughness of precision surfaces.

With the revision of the SI in 2019, the Consultative Committee for Length (CCL) of the International Committee for Weights and Measures published a secondary method for realising the SI metre in terms of a new, agreed value of the lattice spacing of crystalline silicon. This value, based on SI-traceable X-ray diffraction measurements, has a standard uncertainty of a few attometres ( $10^{-18}$  m)<sup>1</sup>. For AFM calibration, the CCL secondary method includes recommended values for the heights of monoatomic lattice steps that can self-assemble on the surface of slightly mis-cut crystalline silicon during annealing under ultra-high-vacuum conditions. These recommended values, for measurement under ambient conditions of monoatomic (100) and (111) orientation lattice steps, have a standard uncertainty of 7.5 pm<sup>2</sup>. A major contribution arises from the uncertainty in the homogeneity of the native SiO<sub>2</sub> surface layer.

In principle, this approach allows any operator of an AFM with access to a monoatomic silicon lattice step structure to calibrate the vertical axis of their instrument at the sub-nanometre level directly against a realisation of the SI metre. The accuracy of the calibration, however, is strongly dependent on how an image of a silicon lattice step is processed and analysed in deriving a measurement of the step height.

We demonstrate image processing and analysis methods used to derive lattice step height values, and associated measurement uncertainties, from images of a silicon (111) surface with lattice steps in a “staircase” configuration. We compare the performance of three commonly used image processing and analysis software packages: the Scanning Probe Image Processor (SPIP™) from ImageMetrology SA, the open source Gwyddion, and MountainsSPIP from Digital Surf.

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# Functional, micrometer-thick zinc oxide coatings for the catalytic generation of nitric oxide from prodrugs

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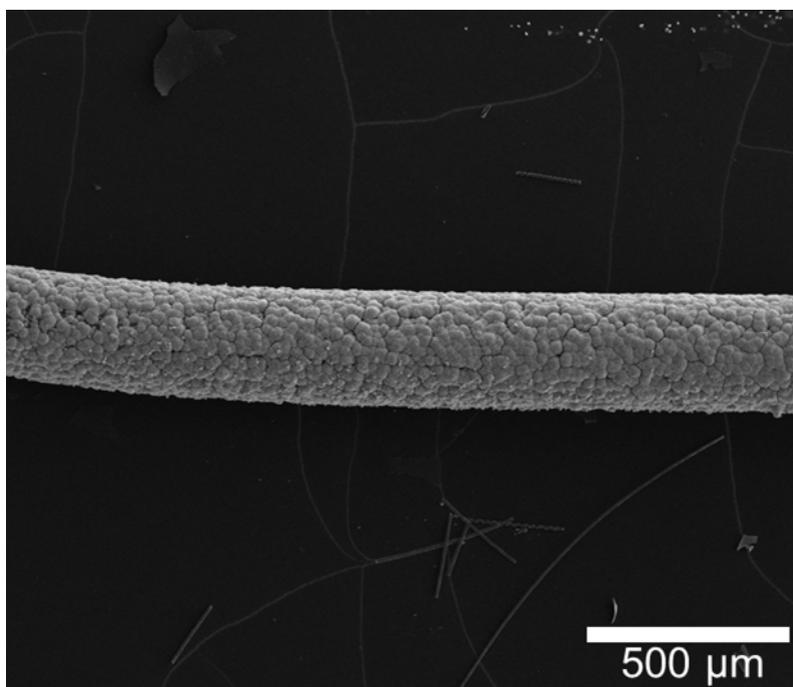
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Nitric oxide (NO) is a potent biological molecule that contributes to a wide spectrum of physiological processes. However, the potential of NO as a therapeutic agent is limited by its short half-life in human tissues. A new strategy to deliver NO relies on in-situ decomposition of NO prodrugs by zinc oxide (ZnO) particles.<sup>1</sup> However, a translation of this technology to the clinic will require the ability to coat medical devices (e.g. metallic stents) with ZnO coatings of the desired thickness and surface roughness.

This study presents a systematic investigation of how three ZnO precursors (urea, sodium hydroxide and hexamethylenetetramine) can produce coating of widely different homogeneity and roughness, based on the synthesis conditions (temperature and concentration) and the metal substrate (titanium, steel and cobalt-chromium alloy). These differences are explained based on the classical nucleation theory and the different surface energies of the substrates. The kinetic of NO generation and the influence of ZnO thickness is also investigated.

In conclusion, this study provides a general strategy for the preparation of micrometer-thick ZnO coatings, which can be used for the in-situ generation of NO.



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# The potential role of asymmetry in the origins of primitive cell motility

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Vesicles self-assembled from fatty acids are one of many models researchers use to mimic compartments preceding live cells on prebiotic Earth.<sup>1</sup> These protocells were rudimentary and would have lacked the protein organelles that enable motility for ensuring their survival. We explore one possible mechanism of autonomous protocell movement *via* diffusiophoresis in such protocells, whereby the protocell may actively move in a liquid medium as a result of a self-induced local chemical gradient.<sup>2</sup> We also explore using active propulsion to generate motion. This involves encapsulating catalytic nanoparticles within the vesicle, inducing asymmetry in the vesicle structure and catalysing a reaction inside the vesicle to generate propulsion. Optical microscopy allows for motion tracking of these vesicles, and then quantitative analysis to classify the type of motion observed.

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## Effect of pH on the packing and properties of fatty acid bilayer membranes

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The ability of fatty acids to self-assemble into a variety of morphological structures has been well established in literature. One such structure is giant unilamellar vesicles (GUVs) which self-assemble at a pH slightly below the apparent  $pK_a$  of the fatty acid.<sup>1</sup> These GUVs are extremely sensitive, with small changes in pH and salt concentration dramatically affecting self-assembly.<sup>1</sup> Simulation results show that these changes in self-assembly are due to changes in the packing of fatty acid molecules. With a slight increase in deprotonation, fatty acid bilayer membranes become more disordered and undergo a reduction in hydrogen bonding. Using electrical impedance spectroscopy and turbidimetry, we find that these changes in packing also affect the permeability of the membranes and their propensity to rupture.

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# Understanding and optimisation of Chitosan based hydrogels for 3D printing

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3D printing promises to provide a significant breakthrough in the field of tissue engineering. However, the primary limitation of biomaterials ink/bioink inventory and lack of clarity around a unified systematic screening for the development of biomaterial inks have frequently been cited as a major issue that limits its potential. The present study tries to address this by developing a biomaterial ink composition while outlining a framework for evaluating printability for extrusion-based printing. The developed biomaterial ink is based on a photo-curable chitosan (ChiMA) and methyl cellulose (MC), with the latter serving as a rheological modifier (Figure 1). An 'ideal' ink should satisfy both biological and physical/mechanical requirements of the printing process. To check these requirements, potential ink formulations were made and evaluated using three screening tests on flow properties, physicochemical properties, and layer stacking ability. Two ink formulations out of an initial twelve were further analysed for their rheology, degradability, print evaluation and preliminary cytocompatibility, leading to a candidate biomaterial ink formulation. In addition, a printability assessment demonstrated the candidate ink's excellent shear thinning, rapid gelation and ability for retention of the structural integrity until post curing, confirming its utilization in extrusion based 3D printing. This printability assessment was combined with a previously developed mathematical model to narrow down the ideal operating parameters of the extrusion printing by calculating the extrusion velocity using the shear thinning coefficients and printer operating variables (Pressure, needle dimensions). Formulated inks printability was then demonstrated by printing geometries with versatile shapes such as star shape and circles. The scaffolds printed with ChiMA/MC inks showed adequate cytocompatibility for human dermo fibroblasts but with limited matrix adhesion and proliferation.

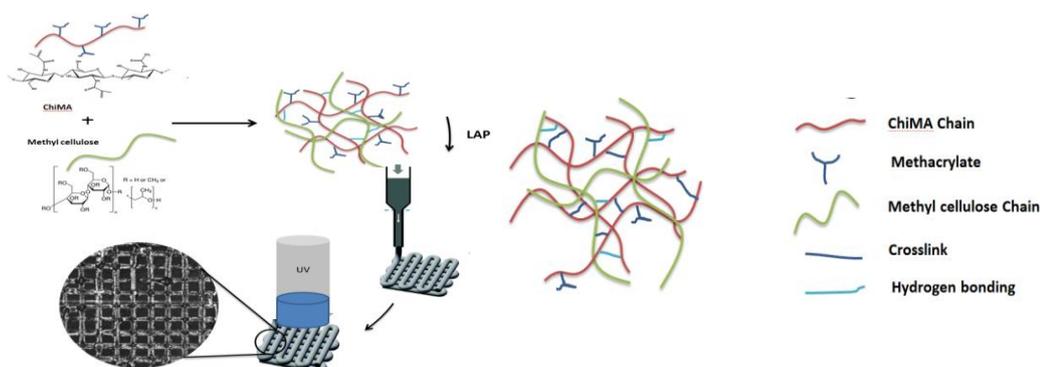


Figure 1 Schematic representation of ChiMA (methacrylamide chitosan)/methyl cellulose biomaterial ink development.

# Self-Assembly of Carbon Dioxide Nonionic Surfactants in Ionic Liquids

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The diverse intermolecular interactions present in ionic liquids (ILs), and especially protic ionic liquids, generates a solvophobic effect that can give rise to a striking amphiphilic nanostructure consisting of sponge-like interpenetrating networks of polar and apolar domains,[1] and also makes them excellent media for surfactant self-assembly.

Previous studies of polyoxyethylene alkyl ether nonionic surfactants,  $C_nE_m$ , in ethylammonium nitrate (EAN) and propylammonium nitrate (PAN) have shown they can support the full range of amphiphilic self-assembly behaviour of nonionic surfactants for various applications.[2-4] However, the head group of the workhorse nonionic surfactant, ethylene oxide (EO) is a petrochemical product, prompting researchers to seek bio-renewable substitutes, amongst which carbon dioxide stands out. Recent studies of nonionic surfactants incorporating  $CO_2$  (partly substituted for EO, Figure 1) have shown they are promising surface-active molecules.[5, 6] This study is directed at understanding self-assembly behaviour of  $CO_2$  nonionic surfactants in ILs. Specifically, we will examine the structure of surfactant-IL solutions using small angle neutron scattering in order to determine how IL nanostructure affects the properties and morphologies of surfactant aggregates.

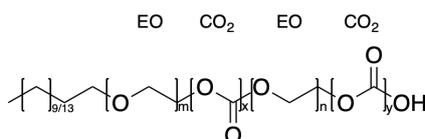


Figure 1. Structure of  $CO_2$  nonionic surfactants, the headgroup is a random copolymer of  $CO_2$  and ethylene oxide units.

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# RAPID RELAXATION NMR MEASUREMENTS TO PREDICT RATE COEFFICIENTS IN IONIC LIQUID MIXTURES

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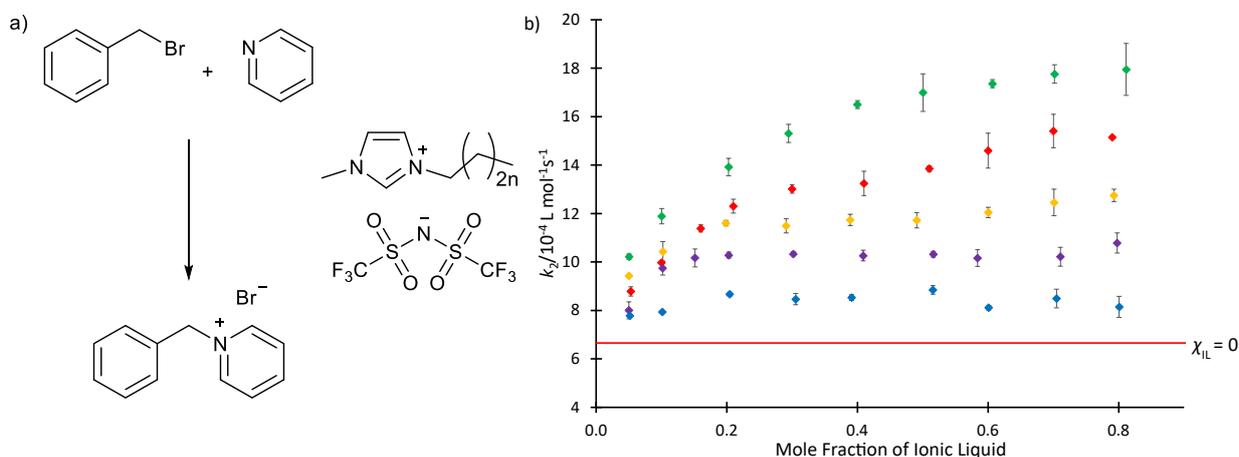
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Ionic liquids have been investigated as a potential replacement for molecular solvents due to their unique properties and customisability.<sup>1</sup> Despite this, common application remains inaccessible due to their often unpredictable effects on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

The reaction between pyridine and benzyl bromide has been investigated in mixtures of acetonitrile and different ionic liquids in the 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ( $[C_{2n+2}C_{1im}][NTf_2]$ ,  $n = 0-5$ ) homologous series (Fig. 1a). Unique behaviours as a function of mole fraction were seen in each ionic liquid, along with a consistent trend where longer alkyl chain substituents result in lower values of  $k_2$  (Fig. 1b).



**Figure 1.** a) (left) the reaction of benzyl bromide and pyridine, performed in the presence of the  $[C_{2n+2}C_{1im}][NTf_2]$  homologous series of ionic liquids ( $n = 0-5$ ). b) (right) mole fraction dependence of the bimolecular rate coefficient ( $k_2$ ) for the reaction of benzyl bromide and pyridine at 22.2°C in mixtures containing different proportions of either  $[C_2C_{1im}][NTf_2]$  (◆),  $[C_4C_{1im}][NTf_2]$  (◆),<sup>3</sup>  $[C_6C_{1im}][NTf_2]$  (◆),  $[C_8C_{1im}][NTf_2]$  (◆), or  $[C_{12}C_{1im}][NTf_2]$  (◆) with acetonitrile, and in acetonitrile (—). Errors are reported as the standard deviation of at least triplicate results. Some errors fall within the size of the markers used.

Solvent relaxation NMR measurements are sensitive to both molecular motion and solvent structuring, with entropic differences such as increases in structuring having a large influence on the value of the spin-spin relaxation time ( $T_2$ ). Since the observed increase in  $k_2$  is entropically influenced,  $T_2$  of the homologous series of ionic liquids was investigated. Correlation of  $T_2$  and  $k_2$  allows quantitative prediction of rate coefficients in various solvent mixtures, including ionic liquids not part of the initially considered homologous series. These data, along with associated activation parameters, indicate that solvent structuring plays an important part when understanding the microscopic origins of rate enhancement for these ionic liquid systems.

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# Machine-Learning based in-line holography for localization of weak scatterers in presence of noise

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How to image objects in a crowded environment? Digital in-line holographic microscopy (DHM) is a non-invasive optical modality that encodes three-dimensional (3D) information about the microscopic scatterers (Fig. 1a), captured in real time on fast sensors i.e., CCD and CMOS cameras. Processing and analysis of these recorded holograms can be done using a user-friendly Python interface<sup>1</sup> which is based on Lorenz-Mie scattering theory. DHM can be used to localize and quantify the motion and interaction of scatterers, and to quantify diffusion.

The challenge lies in fact that in DHM, the scatterer with a large cross-section area dominates the scattering process – particularly in crowded environments such as biological tissues. Therefore, it is difficult to extract information (about the weak scatterer) from holograms containing the interference from both weak (signal) and strong (noise) scatterers.

We propose a data driven approach based on conditional generative adversarial networks (cGANs). We train cGANs on simulated image-pair data consisting of holograms of (A) weak scatterers only and (B) weak + strong (hybrid) scatterers (see Fig. 1(b)). We then demonstrate that the model trained on these image pairs can efficiently negate the effect of strong scatterers from the unknown hybrid holograms (see Fig. 1(c)). This decoupling then allows us to study the interaction and motion of these weak scatterers.

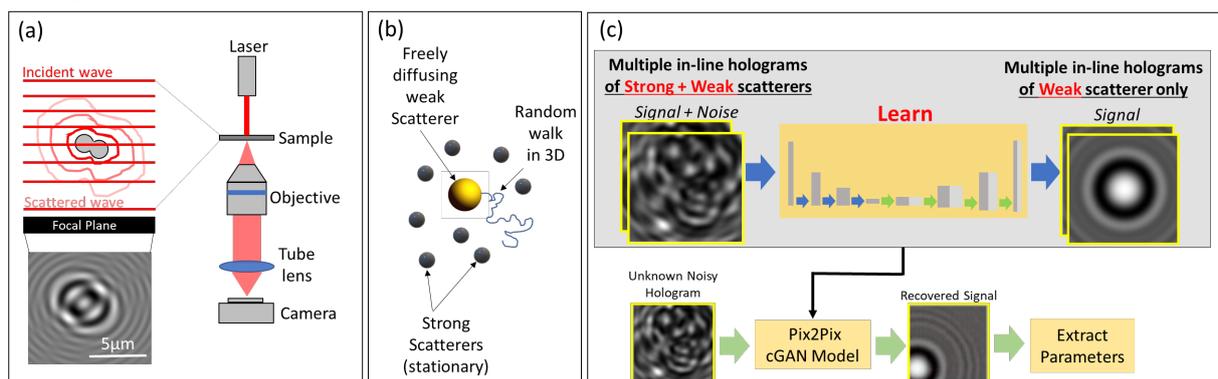


Fig1. (a) In-line holography setup<sup>1</sup>; (b) scheme for generating simulated in line holograms in HoloPy<sup>1</sup>; (c) Implementation of cGANs to get a standalone model for parameter extraction.

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## Fibrin clot structure is mediated by biomaterial wettability

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Cardiovascular medical device thrombosis is associated with poor patient outcomes. Adsorption of prothrombotic proteins such as Factor XII (FXII), fibrinogen, von Willebrand Factor (vWF) and complement proteins influence the cascade of events which follow and thus the nature of the thrombi formed<sup>1</sup>. It is well established that activation of the intrinsic pathway of coagulation, specifically activation of factor XII (FXIIa), is of particular importance. FXIIa has been shown to preferentially generate on hydrophilic, negatively charged materials and has been associated with faster coagulation i.e. fibrin clot network formation. Fibrin clot structure has emerged as an important factor which is altered in plasma from patients with pro-thrombotic diseases including coronary artery disease. However, the influence of medical device material properties on the ultimate fibrin clot structure and thus functional consequences are unknown.

We used the hydrophobic polymer polystyrene (contact angle 90°) and surface modification using oxygen plasma to render the polystyrene hydrophilic (contact angle 15°) to investigate the effect of material wettability on FXIIa activity, coagulation time, and fibrin clot structure. This surface modification was associated with increased surface oxygen content without substantially altering surface roughness. In line with previous literature, surface hydrophilicity increased FXIIa activity in platelet-poor plasma (PPP) and caused faster coagulation in static conditions. Fibrin clot networks occupied increased volume and consisted of increased fibrin fibre density on hydrophilic polystyrene. These clots were more resistant to fibrinolysis, compared to hydrophobic polystyrene. Finally, we demonstrated dependence of these findings on FXIIa using the FXIIa-inhibitor corn trypsin inhibitor.

These findings have implications for the selection of materials for use in the fabrication of future cardiovascular medical devices. Furthermore, material wettability could be purposefully manipulated to influence clot structure for fibrin-based biomaterials.

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# Surface Chemistry of Cellulose affects its Mucoadhesivity in the Development of Epidemic Thunderstorm Asthma (ETSA)

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The inhalation of biological aeroallergens (e.g. pollens) are known to cause allergic rhinitis and asthma<sup>1</sup> by triggering a cascade of immune reactions<sup>2</sup> that often worsen the symptoms. ETSA is a rare type of asthma that is believed to be caused by the inhalation of thunderstorm-borne pollen grains affecting thousands of individuals within a short span of time<sup>3</sup>. In this work, we investigate the fundamental physicochemical basis of the phenomenon. We demonstrate a model system to investigate concerned biointerfacial interactions such as cellulose-mucin interactions mimicking pollen coat and air-way mucosa. Furthermore, we mimicked thunderstorm conditions by generating air-plasma (AP) and plasma-activated water (PAW), examined its effect on surface chemistry of cellulose, and its subsequent interactions with mucin. Quartz Crystal Microbalance with Dissipation (QCM-D), and Neutron Reflectometry (NR) techniques showed that AP and PAW treatment changes the mucoadhesivity of cellulose<sup>4</sup>. Our analysis reveals that both AP and PAW affect the surface chemistry of cellulose by making it highly hydrophilic and slightly hydrophobic, respectively. The mass adsorption and layer thickness profile of mucin on plasma-treated cellulose indicates its non-specific interactions with cellulose and bio-adhesive nature. Interestingly, our in-depth NR analysis manifests the conformational alteration in mucin on different AP and PAW-treated cellulose surfaces, which provides structural insight into mucin interactions with inhaled particles.

In this talk, we will describe the model system for studying cellulose-mucin interactions at sub-nanometre scale, and factors affecting adsorption of mucin on different plasma-treated surfaces. We anticipate that our results will not only help in the constructive understanding of initial biointerfacial interactions contributing to the development of thunderstorm asthma but also provide benchmark for effective treatment of ETSA.

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## Small Angle Neutron Scattering instrument Bilby: capabilities to study mainstream and complex systems

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ANSTO for more than ten years successfully operates Small Angle Neutron Scattering (SANS) instrument Quokka<sup>1</sup> and in 2016 commenced user operation of the second SANS instrument, Bilby<sup>2</sup>. Ultra-small angle scattering machine Kookaburra<sup>3</sup> is completing the set of the SANS instruments at ANSTO.

Bilby exploits neutron Time-of-Flight (ToF) to extend the measurable Q-range, over and above what is possible on a conventional reactor-based monochromatic SANS instrument. In ToF mode, the choppers are used to create neutron pulses of variable (~3% – 30%) wavelength resolution.

Two arrays of position sensitive detectors in combination with utilizing of wide wavelength range provide capability to collect scattering data of wide angular diapason without changing experimental set-up (maximum accessible Q on the instrument is 0.001-1.8Å<sup>-1</sup>). Additionally to the ToF, Bilby can operate in monochromatic mode.

The question is how the advanced design features can be applied to the real scientific questions. In short, having large dynamic range available in one go, opens up a possibility to study complex system, like micelles and hierarchical materials. Additionally, there is a range of sample environment available allowing to change conditions in situ, which is priceless for study a range of samples stretching from colloids to metals. In my presentation I am giving several examples demonstrating how ToF SANS can bring light to structural changes of the surfactant wormlike micelles structure under various conditions. Also, study of the hard matter physics examples will be presented.

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# Large boundary slip at lubricant-infused surfaces

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The interaction between liquid flows and solid surfaces has become an important issue for the manipulation of fluids at small scales<sup>1</sup>. Frictional drag, which arises as to the direct consequence of this solid-fluid interaction, accounts for a great part of the energy invested in the transport of fluids. Lubricant-infused surfaces (LIS)<sup>2</sup>, in which an immiscible liquid is trapped within the surface texture, minimise the contact of the liquid with the solid substrate and, therefore, reduces the hydrodynamic drag significantly. This drag reduction is normally explained as an apparent slip of the fluid due to the mobility of the lubricant and is proportional with the lubricant height  $h_0$  and the ratio of the viscosity of the flowing liquid over that of the lubricant  $\mu_w/\mu_o$  (see Fig.1). Here, using highly accurate microfluidic measurements, we confront these predictions with experimental observations conducted on a nanostructured wrinkled Teflon surface<sup>4</sup> infused with silicone oil or hexadecane. We found that at low viscosity ratios  $\mu_w/\mu_o < 1$ , the drag reduction is 50 times higher than predicted. Although this disagreement has been observed in previous studies, no explanation has been proposed up to now. In this study, using atomic force microscopy and confocal microscopy, we found that the nucleation of pancake-like nanobubbles on these surfaces is responsible for the large slippage observed in these systems.

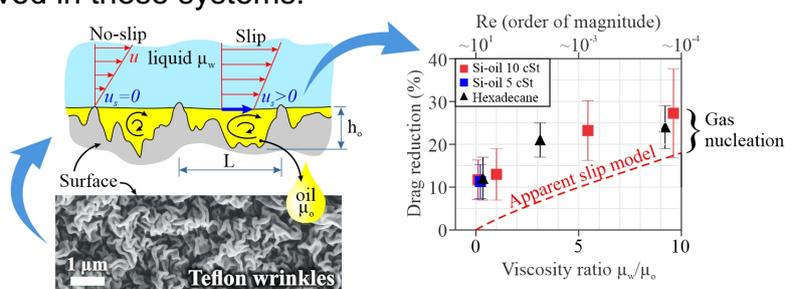


Figure 1: Wrinkled Teflon surfaces are infused with oil and test under flow.

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# Self-Assembly Behaviour of Janus Nanorods

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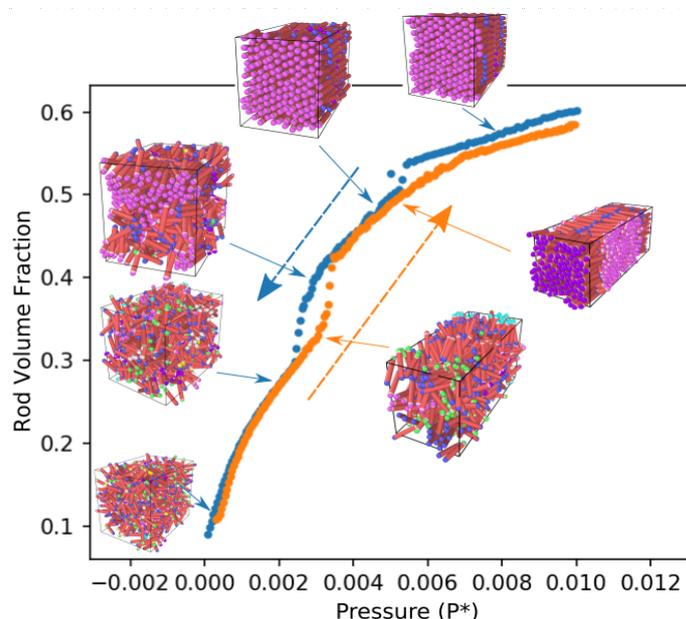
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Janus nanoparticles have two chemically distinct faces, typically one repulsive and one attractive. Because of their inherent anisotropy they have quite complicated phase behaviour and can act as surfactants depending on the interactions of each face.<sup>1</sup>

We have used computer simulations to study the self-assembly behaviour of Janus nanorods which have one attractive end and one repulsive end. By varying the interaction strength, pressure, and length of the attractive portion, we are able to produce a wide range of assembled structures including lamellar bilayers, tubular micelles, smectic A, crystal, frustrated bilayers and spherical micelles. The transition between some of these structures appears to be barrierless.



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## Soft-Hard Janus Nanoparticles for Polymer Encapsulation

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We demonstrate a scalable continuous feed method for the synthesis of polymer Janus nanoparticles with different composition and aspect ratios between lobes, including with one hard cross-linked polystyrene lobe and one soft film-forming poly(methyl methacrylate-co-butyl acrylate) (P(MMA-co-BA)) lobe, through emulsion polymerization. The Janus nanoparticles with the soft P(MMA-co-BA) lobes can spontaneously self-assemble around solid particles in an aqueous phase, forming a thin polymer film. The process is achieved at room temperature and under mild conditions. The Janus nanoparticles show excellent encapsulation ability for a variety of solid particles, such as organic and inorganic pigments, carbon nanotubes and calcite, without requiring polymerization.<sup>1</sup> The role of the surface charge of the particles, wettability, and morphology are investigated to explain fundamental questions on the encapsulation mechanism.

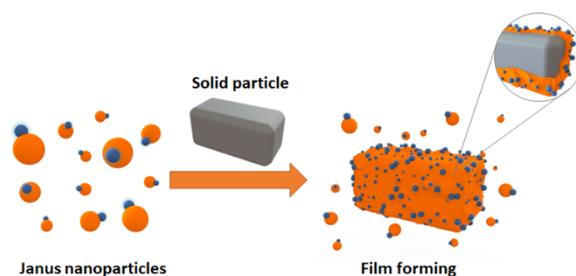


Figure 1. Schematic of encapsulation of particles in aqueous phase by film forming Janus nanoparticles

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# Formation of Binary Nanorod Superlattices

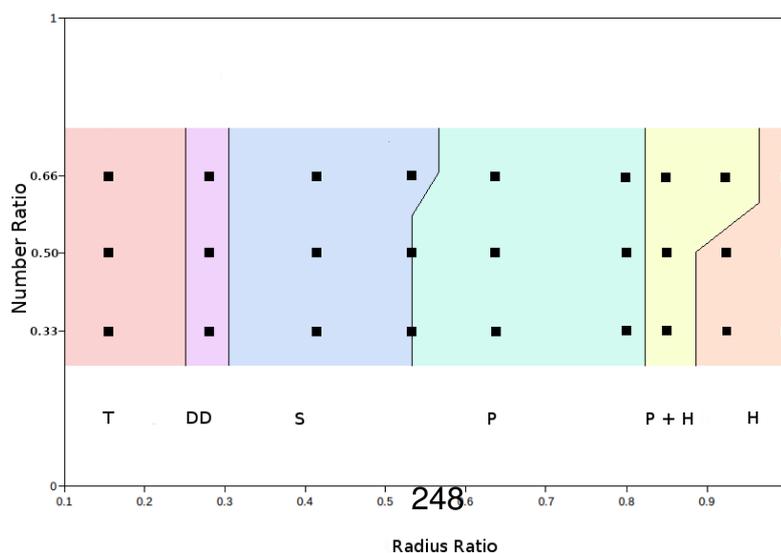
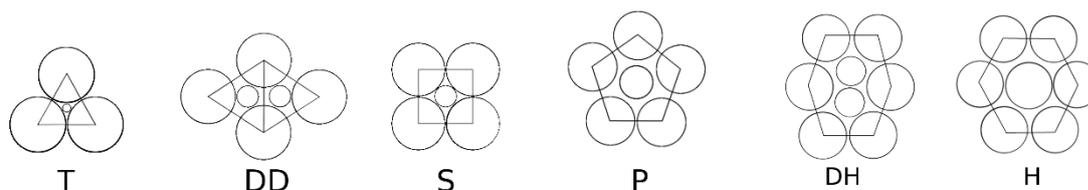
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Solar power in highly urbanised settings is limited due to the pervasiveness of high-rise buildings with limited roof space available for solar power generation. However, the facades of these buildings are often mainly comprised of windows which could be utilised in a Luminescent Solar Concentrator (LSC). LSC's utilise total internal reflection to direct light to their edges for solar harvesting. These systems can also be built as nearly transparent allowing windows to be still used. A limitation on LSC's is the low efficiency of these systems. But, by controlling the assembly of nano-luminophores in the wave guide it is possible to increase their efficiency.

In this paper the packing of rounded rods in 3D space is examined for the purpose of designing an improved LSC wave guide. This is achieved through simulating Brownian dynamics with the LAMMPS molecular dynamics package. Several orderings of binary rods are observed both with entirely attractive and mixed interaction regimes. Some of these orderings are as predicted from hard disc packings, but new pentagonal orderings are observed as well. These results are also examined through calculating coordination. From these simulations it is observed that the correct number ratio is important to form an extended lattice. Additionally, it is determined that mixed interactions are required to prevent separation of the two rod types within a lattice into separate phases. From these discoveries, goals for future experimental studies in this area have been more clearly defined



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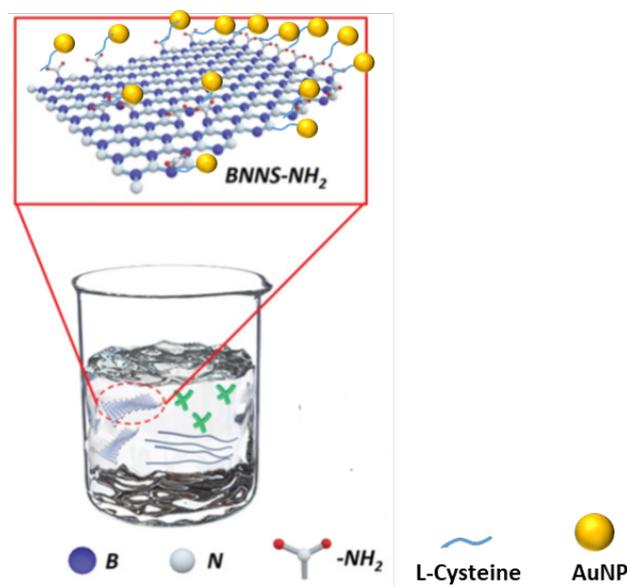
# Understanding and Controlling Surface Chemistry of Boron Nitride Nano-sheets

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Boron Nitride Nano sheets (BNNS) are currently among the most promising and popular two-dimensional (2D) material. BNNS are typically up to a few atom thick layer(s) of a bulk form[1]. The properties like chemical [2] and thermal [2] stability, biocompatibility [2] and its unique mechanical [3] and electrical [3] properties, makes it a promising candidate for various applications. However, the chemically inertness [2] and oxidation resistance of BNNS [2] makes it difficult to be functionalized and therefore hard to disperse in aqueous solutions. Herein, we use simple techniques (synchronizing the surface charges) and methodologies (UV-Vis-NIR spectroscopy) for improving the functionalisation and characterization of BNNS respectively. This work showcases simple and efficient techniques to step forward our understanding of BNNS surface chemistry.



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# Protein surfactant-enabled functional droplets with customizable shape controlled by microfluidics

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Emulsion droplets with well-controlled size, structure, chemical properties can serve a multitude of purposes in material science and industrial applications. Micro-scale droplets have been widely applied as encapsulation entities, miniaturized reactors, and analytic platforms owing to their unique multi-phasic, compartmentalized structure and small volumes<sup>1-2</sup>. Herein we report a rare 'shape-memorable' oil-in-water droplet formulation that is stabilized by a polyethylene glycol (PEG)-modified protein-surfactant, the developed droplets are very stable against coalescence and can maintain non-spherical shapes including monodisperse ellipsoidal droplets with aspect ratios ranging from 1.0 to 3.4. In-depth investigation regarding the mechanical properties of different protein networks were conducted to elucidate the mechanism behind the shape conservation phenomenon. The dynamic rheological properties of protein-accumulating interfaces were explored by microfluidics, showing that PEGylated protein films at interfaces have an enhanced resistance to flow shearing compared with non-PEGylated counterparts, which supported our hypothesis that a highly elastic mechanically stronger interfacial films were formed through the use of the PEG-modified protein. Moving a step forward, we demonstrated the possibility of functionalization of the droplet interface by incorporating biotin as an example, which revealed the potential of customizing droplet interfaces on-demand using surface-active protein as an anchor for integrating functional moieties. These functional non-spherical oil droplets with tuneable surface properties may offer new opportunities for chemical synthesis, controlled release, sensing and other applications.

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# Fibrinogen and Bovine Serum Albumin Adsorption and Conformational Dynamics on Silica Nanoparticle Based Model Substrates

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The development of materials for medical devices, including implants, stent and pacemakers and other medical consumables, remains a challenging research area due to the immediate adsorption of proteins onto biomaterial interfaces. Because of the higher surface activity of proteins, this initial protein adsorption occurs rapidly and may prevent other favourable biological interactions.<sup>1-2</sup> This is particularly an issue for surfaces that come into contact with blood, often resulting in blood coagulation, thrombosis and inflammation.<sup>3</sup> 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 at biomaterial interfaces.

In this research, silica nanoparticle-based coating was used as a model 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. The silica coatings were functionalized with a series of common surface chemistries using silanes having specific functional groups (–OH, –CH<sub>3</sub>, –NH<sub>2</sub>, –COOH and –F). Fibrinogen and albumin were used as model proteins, as these proteins have been commonly used over decades to study protein adsorption on biomaterial surfaces.

The presentation will show structural-dynamic processes of single protein molecules on the above silica nanoparticle-based coatings, revealed by the HS-AFM observations of initial protein adsorption.

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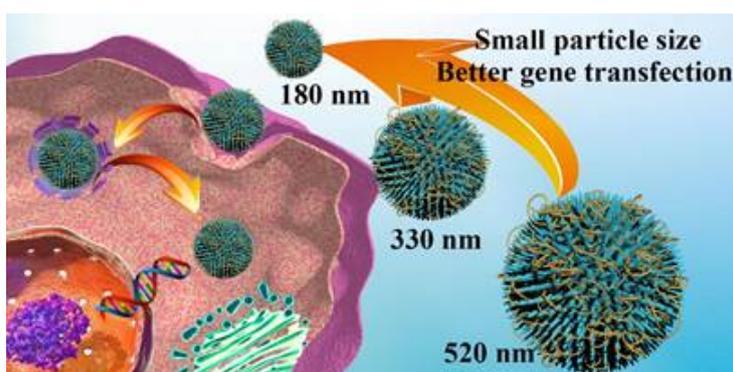
# The Impact of Particle Size on Plasmid DNA Delivery in Silica Nanoparticles Designed with Spiked Nanotopographies

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Silica nanoparticles (SNPs) have attracted widespread attention as biocompatible and efficient nanocarriers for gene delivery. The physicochemical properties of SNPs such as particle size, pore size, nanotopography and surface chemistry play important roles in regulating the intracellular delivery performance of genetic molecules. SNPs engineered with a rambutan-like spiky surface (Ram-SNPs) have shown significantly enhanced transfection efficiency for plasmid DNA (pDNA).<sup>1</sup> However, the impact of the particle size of Ram-SNPs on their pDNA delivery performance has not been previously reported. Here, we synthesized Ram-SNPs with tailored nanoparticles sizes of 180, 330 and 520 nm by controlling the polymerization of resorcinol-formaldehyde and silica in a surfactant free synthesis system. The polyethylenimine modified Ram-SNPs were loaded with pDNA molecules for intracellular delivery. Smaller sized Ram-SNPs demonstrated slightly weaker binding with pDNA, enhanced cellular uptake and significantly higher transfection efficiency than the larger particles. This structure-function relationship is different from other SNPs used for pDNA delivery. The cellular uptake mechanism by Ram-SNPs was also investigated. These findings provide useful guidance for the rational design of silica-based non-viral vectors for efficient gene delivery applications.



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# Bio-inspired design of double network hydrogels with force-mediated molecule release

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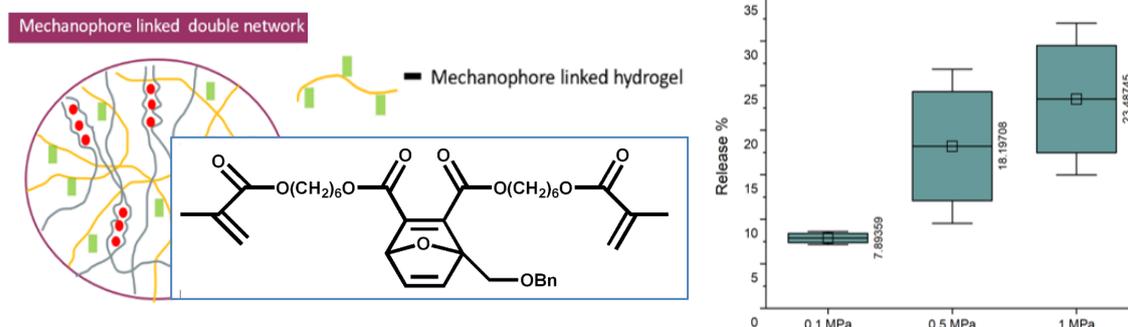
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In biology, forces play a crucial role and are responsible for regulating a wide array of functional activities. For example, cells in the body are exposed to mechanical forces through adhesions to neighboring cells, and the extracellular matrix (ECM).<sup>1</sup> The Native ECM is a complex hydrogel & natural mechanochemical model. The forces generated in the extracellular matrix can direct the release of growth factors to cells in the surrounding tissues, which catalyses important bioactivities.

We have developed a force-responsive double-network hydrogel design, which releases tethered molecular cargo in response to tension and compression. The flex-activated force-sensitive mechanophore crosslinkers give the hydrogel network a dynamic nature and maintains the overall gel architecture without degradation during successive molecule release steps. The results showed that the gel with 5 wt% mechanophores release 7%, 18% and 23% of molecules under compression of 0.1 MPa, 0.5 MPa and 1 MPa respectively. This work may pave the way to develop force activated biomaterial such as implant coatings, “smart” bandages, contact lenses and soft robotics.



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# Mechanical Properties of Soft Particles from Pipette Ion Currents

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It has been shown that mechanical properties of organs and tissues in the human body can be linked to their biological functions and abnormalities<sup>1</sup>. These findings have increased interest in the field of molecular and sub-molecular biomechanics. Ion Pipette Aspiration (IPA) is a novel technique that characterizes mechanical properties of soft colloidal particles and is particularly suited for this field. IPA uses glass micropipettes and operates by applying suction to capture samples through the tip. Both the deformation and the resultant ion current signature are captured as the sample squeezes through (see Figure). This complementary dataset is then used to derive mechanical properties by applying appropriate models. IPA has been used to determine the mechanics of biological<sup>2</sup> and polymer samples<sup>3</sup>. Currently, polydimethylsiloxane (PDMS) emulsions are being used as test samples in order to build an understanding between sample deformation and ion current signature. Experimental results from IPA can also be compared to those derived from colloidal probe atomic force microscope (AFM). This comparative study aims to comprehensively adapt IPA to the nanoscale.

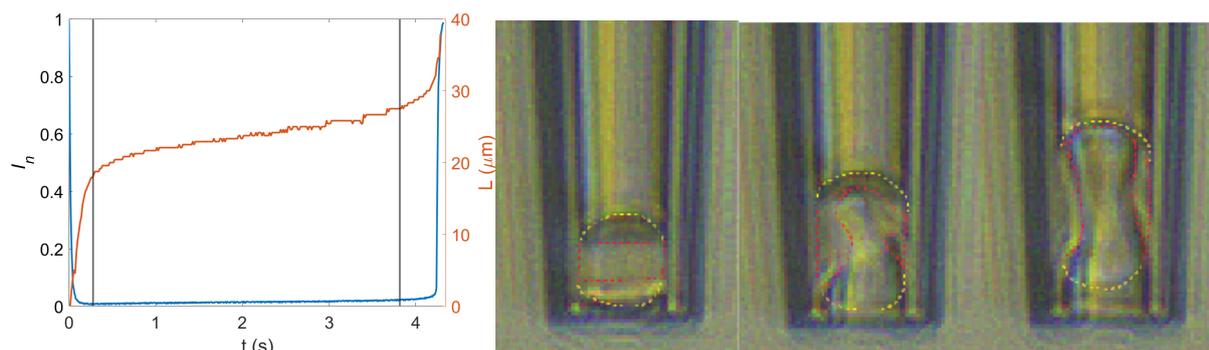


Figure: Left, deformation ( $L$ , red) and ion current ( $I_n$ , blue) histories for a typical IPA event. Right, sequential images of a PDMS particle undergoing IPA, with annotated red and yellow contact lines.

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# Observation of aggregation number and morphological changes in Platonic micelles formed by Surfactin

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## 1, Introduction

Conventional surfactants form micelle in aqueous solution. The aggregation number ( $N_{agg}$ ) of the micelle is about 40~100 and has distribution. The  $N_{agg}$  of micelle is very sensitive to external conditions, for example pH, temperature and salt concentration and continuously changes. On the other hands, our research group found monodispersity in micelles for small  $N_{agg}$ . The number is selected 4, 6, 8, 12, and 20. Interestingly, these numbers match regular polyhedron. We named the micelle as Platonic micelle quoted Plato who is an ancient Greek mathematician. In the region of small  $N_{agg}$ , external condition dependence of  $N_{agg}$  is not revealed. In this research, tracking the  $N_{agg}$  change in the region of  $N_{agg}$  by increasing salt concentration and changing pH. Surfactin (SFNa, Fig.1A) which has cyclic peptide as hydrophilic group was used in this research.

## 2, Result and Discussion

The  $N_{agg}$  of SFNa micelle increase from 12 to 20 via 17 discontinuously by increasing salt concentration while keeping monodispersity. Therefore, the 17mer forms at 10~18 milli molar. But the number of 17 does not match the vertex regular polyhedron. The  $N_{agg}$  of 17 could be explain by Thomson problem which considers the Coulomb potential for calculating the best packing on a sphere with multiple identical spherical caps. Considering the Coulomb potential, coverage ratio which is defined as the ratio of the summation of the cap area to the total surface area of the until sphere has local maximum at the  $N_{agg}$  of 17 (Fig.1B). For these reasons, the 17mer can be stable as the monodispersity micelle at the low salt concentration.

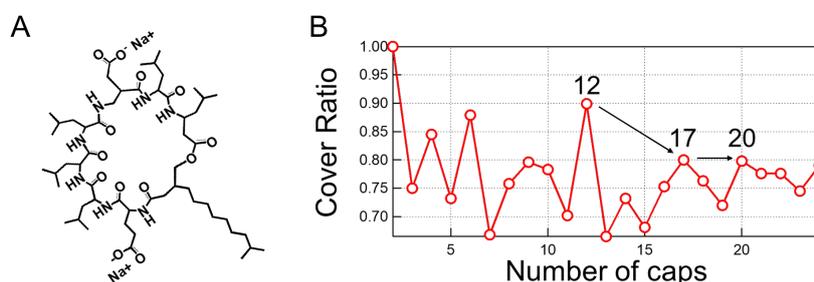


Figure1. (A)Chemical structure of SFNa (B)Cover ratio of the Thomson problem plotted against the number of caps

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# Internalization pathways of microparticles in HeLa cells

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To realize a drug delivery system based on particulate drug carriers, the elucidation of how the particles are internalized into and released from the cells is crucial. So far, we showed that the surface charge of the particles with 1 $\mu$ m diameter affected the internalization amount, and those with positive charge were more internalized.<sup>1</sup> Here, we have clarified the internalization pathways of the particles with positive surface charge and the PEGylated particles that are biocompatible and less toxic.

The 1 $\mu$ m fluorescent silica particles were coated by the polycation (Polyethyleneimine) and were hydrophobized and dispersed in water with Pluronic F127 to obtain the positively charged and the PEGylated particles, respectively. HeLa cells were incubated in the medium with the particles ( $3.5 \times 10^7$  /mL) for 15 min at 37°C, and the fraction of the cells with the internalized particles was evaluated by the laser scanning confocal fluorescence microscope. The dependence of the  $F_{in}$  on various inhibitors was observed to estimate the internalization pathways. As shown in Table 1, the major pathway of the positively charged particles was the energy-independent pathway and the minor one was phagocytosis. The major and minor pathways of the PEGylated particles were macropinocytosis and phagocytosis, respectively.

To investigate the exocytotic activity, after the incubation in the medium with the PEGylated particles for 15 min, HeLa cells were exposed to the particle-free medium for another 15 min. As shown in Fig. 1, the  $F_{in}$  value decreased into half after the exposure to the particle-free medium and 5% of the cells still kept the particles inside. The intracellular transport of the internalized particle is being investigated.

Table 1. Internalization pathways

Pathways	Positively charged particles	PEGylated particles
Macropinocytosis	N.D.	Major
Phagocytosis	Minor	Minor
Clathrin-dependent endocytosis	N.D.	N.D.
Caveolin-dependent endocytosis	N.D.	N.D.
Energy independent pathway	Major	N.D.
Other	Minor	Minor

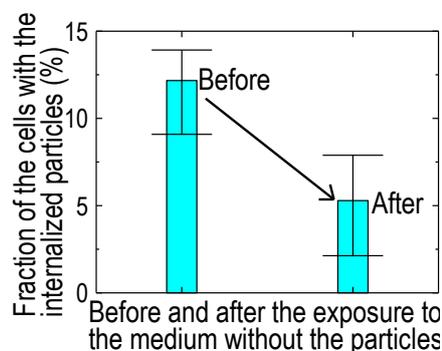


Fig.1. Exocytosis of PEGylated particles.

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# DNA-templated complexation of beta-glucan/Oligo-DNA

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## Introduction

Hybridization of antisense oligonucleotides (AS-ODNs) with target mRNAs results in the inhibition of gene expression by RNase H activation or alternative splicing. AS-ODNs are 20-30 bases in length and are thus long enough to specifically bind to target sequences. It cannot be taken up into the cells and therefore cannot be effective. So, the development of a nucleic acid delivery system specific for target cells is required. The natural polysaccharide schizophyllan (SPG) has a main chain comprising  $\beta$ -(1 $\rightarrow$ 3)-D-glucan and one  $\beta$ -(1 $\rightarrow$ 6)-D-glucan side chain that links to the main chain at every three glucose residues. In our previous report, we have shown that dA40s attached AS-ODNs can form a complex with SPG and this can be taken up by cell expressing Dectin-1(beta-glucan receptor). Recently, during process analysis of GPC chromatogram, we found that complexes are not monodisperse when molecular weight of SPG becomes small. It is considered that a peak occurred centering on the molecular weight. In this study, we focused on structural analysis low molecular weight complexes.

## Results and Discussion

First, we corrected a certain range of the elution time. The fractionated samples were then measured by using GPC-MALS. The molecular weights are 49500, 99000, and 149000, respectively, which are integer-fold from the small molecule side. Surprisingly, the dispersity indexes expressed by Mw/Mn were quite small, at around  $1.01 \pm 0.01$ , compared with those in the original SPG. Presumably, when forming the complex, dA is choosing the best-fit SPG in various length SPG.

## Conclusion

Complexes exist in solution with various sizes because of having one, two or three oligonucleotide molecules. They are also considered to be an effective nucleic acid delivery system for nucleic acid drugs targeting Dectin-1-expressing cells.<sup>1</sup>

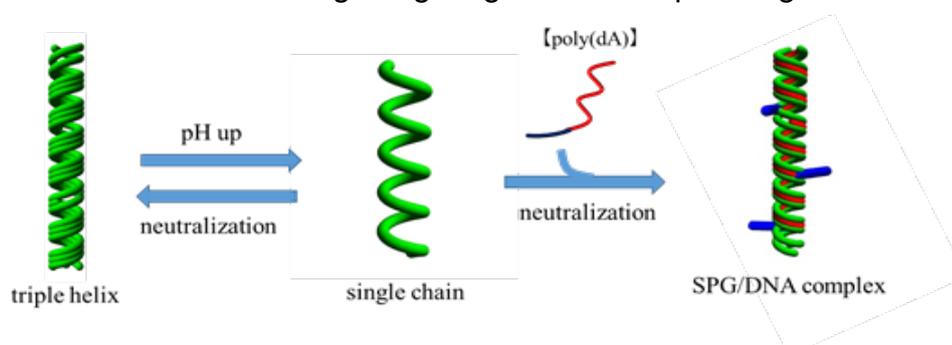


Fig.1 feature of SPG

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# Phosphorylcholine-grafted Molecular Bottlebrush-Doxorubicin Conjugates

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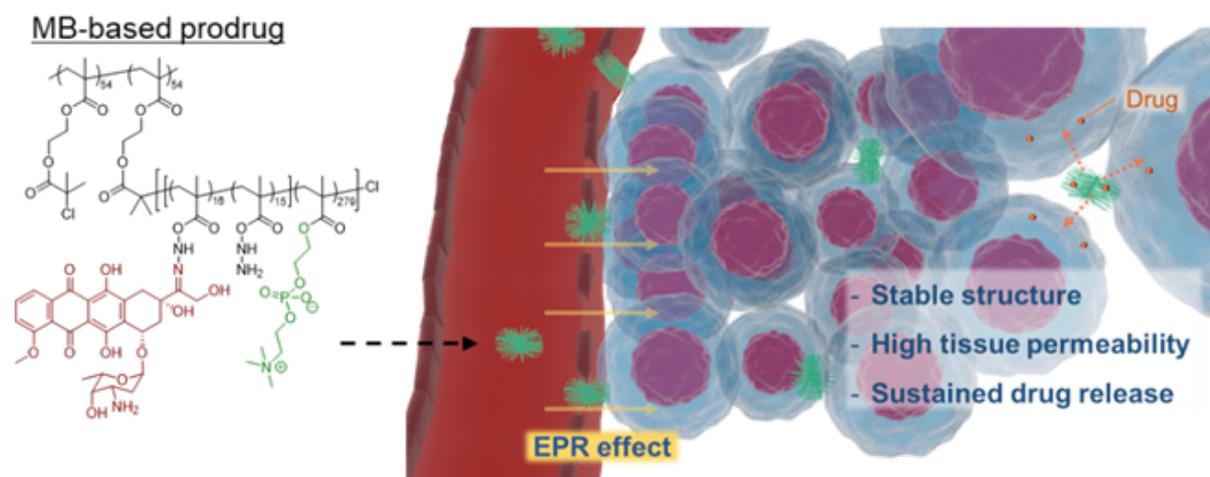
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Controlling the particle structure of tumour targeting nanomedicines *in vivo* remains challenging but must be achieved to control their *in vivo* fate and functions. Molecular bottlebrushes (MBs), where brush side chains are densely grafted from a main chain, have recently received attention as building blocks of polymer-based prodrugs since their rigid structure would be expected to demonstrate high structural stability *in vivo*. Here, we synthesized a poly(methacryloyloxyethyl phosphorylcholine) (pMPC)-grafted molecular bottlebrush (PCMB) conjugated with a cancer drug, doxorubicin (DOX), via an acid-cleavable hydrazone bond. A pMPC-based linear polymer (LP) conjugated with DOX was also prepared for comparison.

We confirmed the lack of structural transition in PCMB between before and after conjugation with DOX using small angle light and X-ray scattering techniques, whereas the structure of LP was significantly influenced by DOX conjugation and transformed from a random-coil structure to a large agglomerate via hydrophobic interactions among DOXs. Although PCMB-DOX and LP-DOX showed comparable tissue permeability, pharmacokinetics, and ability to accumulate in tumour tissues, the antitumour efficacy of PCMB-DOX was better than that of LP-DOX.

We have demonstrated the potential of molecular bottlebrushes as building blocks of drug carriers and believe these findings can contribute to the design of polymer-based nanomedicines.



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# Spontaneous Directional Droplet Motion on Structured Surfaces

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Spontaneous liquid transport has a wide variety of applications, including fog harvesting, microfluidics, fuel cells, and water-oil separation [1,2,3]. Through introducing a wedge-width gradient on solid substrate, droplets can be mobilised by the unbalanced capillary forces [4,5]. Understanding of the droplet movement dynamics on patterned surfaces is important for enhancement of the transport performance. In this work, we develop an energy-based theoretical model describing the movement process of a droplet on surface with the prescribed wedge shape. To check the model, surfaces with different patterns were manufactured by cryo-etching Si wafers using standard photoresists, where spontaneous movement of droplet is achieved (Fig. 1). Good agreement is observed between the theoretical predictions from the model and experimental results. Through theoretical analysis and quantitative comparison between transport performance of different wedge shapes, we identify the key factors affecting the movement process and provide guidelines on wedge shape design for spontaneous directional droplet transport. It is found that wedges with convex edge shapes have the potential of achieving better performance in terms of total travelled distance, compared to the conventional straight wedge designs.

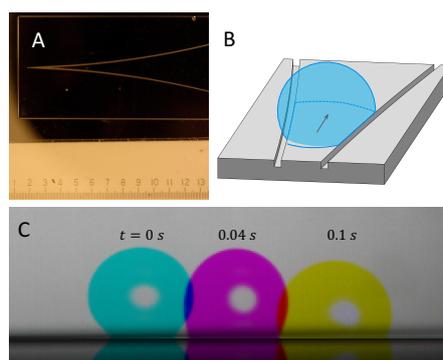


Figure 1. (A) Photograph of top view of curved wedge. (B) Schematic showing the 3D view of a droplet moving in the direction of the arrow on the curved wedge. (C) Side view of 4  $\mu\text{L}$  droplet motion on a curved wedge.

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