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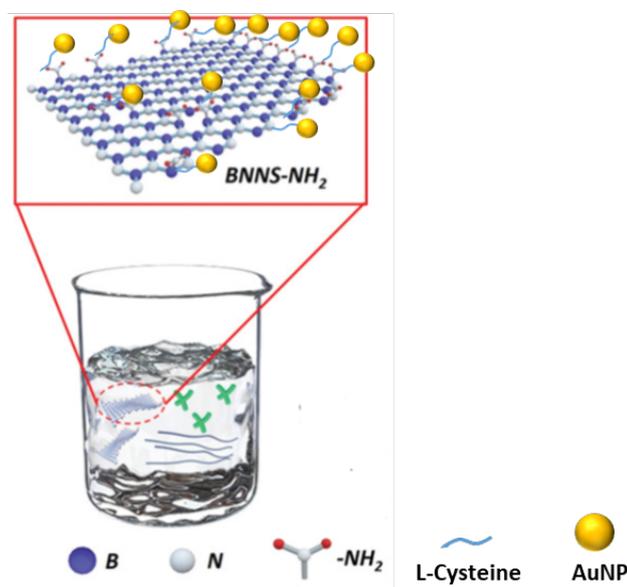
Understanding and Controlling Surface Chemistry of Boron Nitride Nano-sheets

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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 volumes¹⁻². 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.¹⁻² This is particularly an issue for surfaces that come into contact with blood, often resulting in blood coagulation, thrombosis and inflammation.³ 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, –CH₃, –NH₂, –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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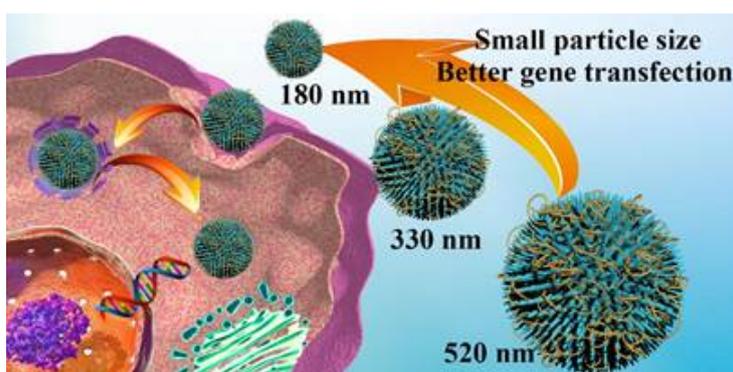
The Impact of Particle Size on Plasmid DNA Delivery in Silica Nanoparticles Designed with Spiked Nanotopographies

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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).¹ 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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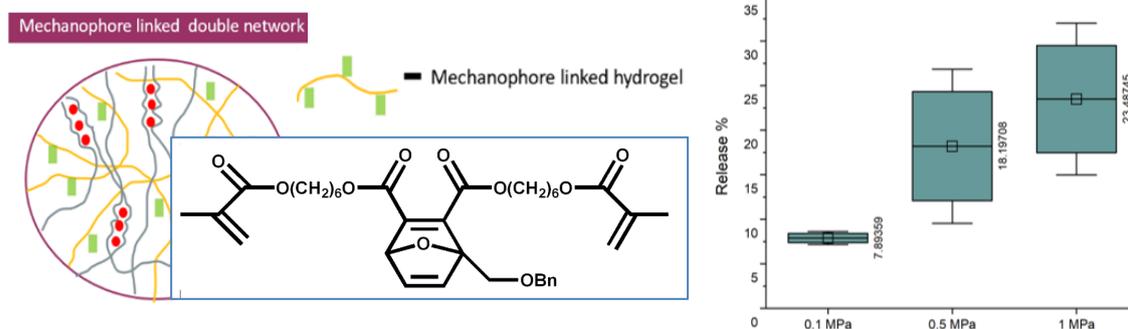
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In biology, forces play a crucial role and are responsible for regulating a wide array of functional activities. For example, cells in the body are exposed to mechanical forces through adhesions to neighboring cells, and the extracellular matrix (ECM).¹ 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 abnormalities¹. 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 biological² and polymer samples³. 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.

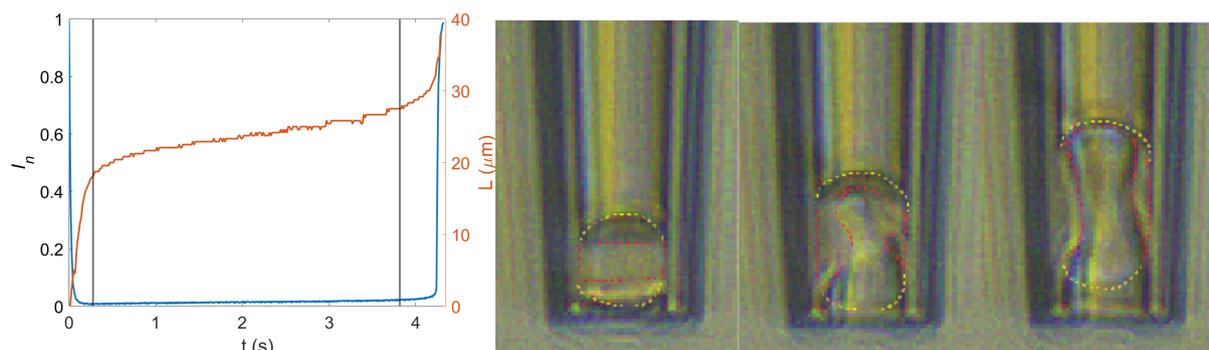


Figure: Left, deformation (L , red) and ion current (I_n , blue) histories for a typical IPA event. Right, sequential images of a PDMS particle undergoing IPA, with annotated red and yellow contact lines.

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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.

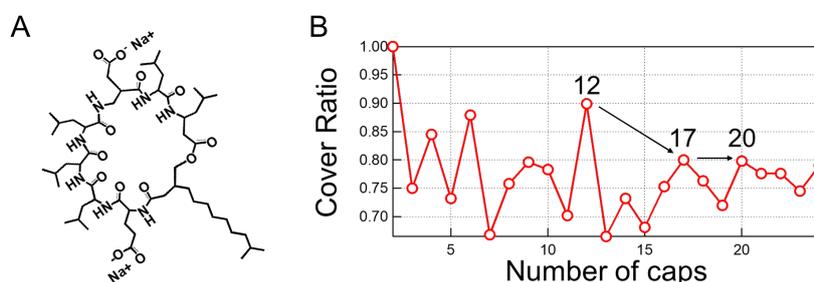


Figure1. (A)Chemical structure of SFNa (B)Cover ratio of the Thomson problem plotted against the number of caps

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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 μ m diameter affected the internalization amount, and those with positive charge were more internalized.¹ 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 μ 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 (3.5×10^7 /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

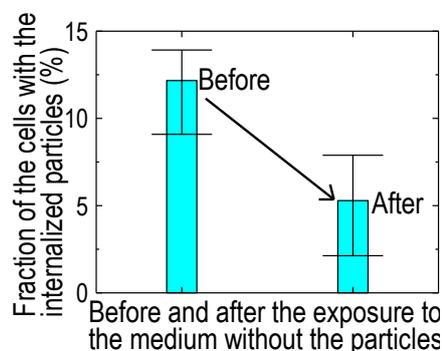


Fig.1. Exocytosis of PEGylated particles.

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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 β -(1 \rightarrow 3)-D-glucan and one β -(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 ± 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.¹

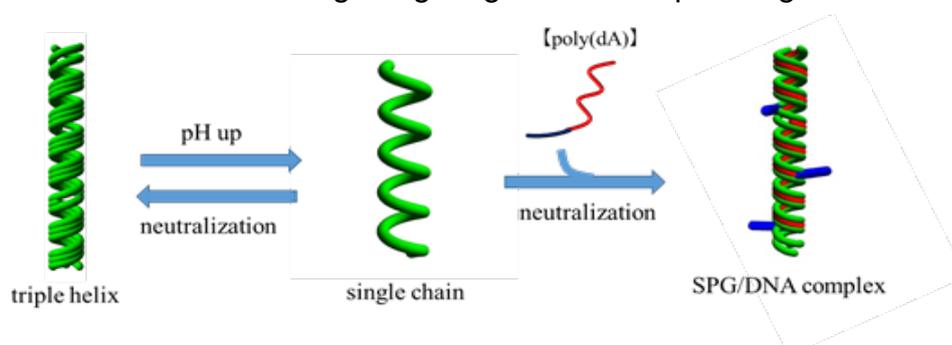


Fig.1 feature of SPG

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Phosphorylcholine-grafted Molecular Bottlebrush-Doxorubicin Conjugates

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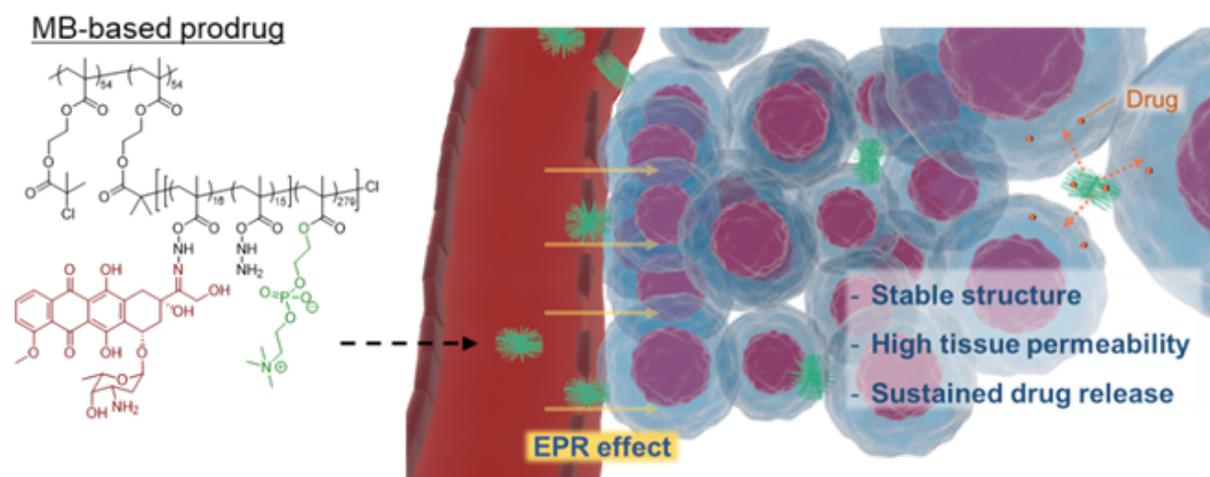
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Controlling the particle structure of tumour targeting nanomedicines *in vivo* remains challenging but must be achieved to control their *in vivo* fate and functions. Molecular bottlebrushes (MBs), where brush side chains are densely grafted from a 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.

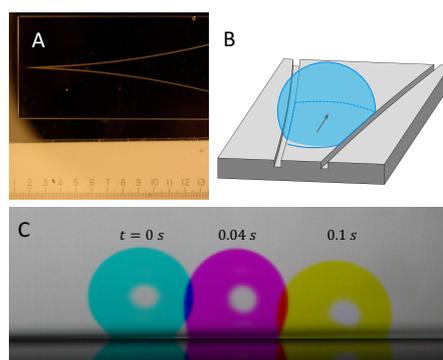


Figure 1. (A) Photograph of top view of curved wedge. (B) Schematic showing the 3D view of a droplet moving in the direction of the arrow on the curved wedge. (C) Side view of 4 μL droplet motion on a curved wedge.

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