Project Description – Project Proposals

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Title: Sessile droplets on switchable lubricant infused surfaces

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Project Description

0. Project summary

Wetting behavior of a droplet on lubricant infused surfaces (LIS) is different from that on solid surfaces due to the presence of a mobile liquid interlayer, a lubricant ridge, and a potential cloaking layer. Although LIS have shown a lot of promising properties, the underlying mechanism of the wetting, movement, and evaporation of droplets on LIS is far from being fully understood. Developing the fundamental knowledge on these behaviors requires both theoretical and experimental tools. This project aims to develop an experimental platform that allows in-situ regulation of characteristic parameters of LIS, including the thickness of lubricant layer on the top, surface morphology, surface tension and viscosity of the lubricant, for studying the main factors manipulating the droplets on LIS. The platform is based on switchable LIS consisting of tunable substrates and responsive lubricants. The tunable substrates consist on either a porous surface or a structured surface with well-defined geometry for stabilizing the lubricant, and of a channel-embedded supporting layer that allows for precise liquid-transport. Responsive lubricants are designed to be sensitive to thermo- or light-stimuli with changes in surface tension and viscosity. We will systematically characterize the switchability of our system in the absence/presence of water droplets by using ellipsometry (< 1 μm) or laser scanning confocal microscopy (> 1 μm) to monitor the change in thickness, using water contact angle to evaluate the variation in surface tension, and using droplet sliding rate to estimate the viscosity. With the calibrated substrates, we will study several basic wetting and relative behaviors on LIS, including 1) the wetting configuration of a droplet on the substrates by in-situ switching the wetting state from Cassie to slippery state, and then to slippery Wenzel state; 2) the evolution of lubricant ridge by changing the thickness of the lubricant layer on the top of LIS and its contribution to the shape and mobility of the droplet; 3) the formation of cloaking layer; 4) the evaporation of a droplet with different lubricant ridge and cloaking layer controlled through the thickness of the lubricant layer and the surface tension of lubricants; and 5) the coalescence of two droplets on LIS by varying the apparent contact angle. These studies will allow us to verify the physical models developed to describe the wetting configurations on LIS, to understand the energy dissipating mechanisms of the lubricant ridge, to develop new understanding on the longevity and stability of LIS, and to provide guiding rule to regulate droplet mixing on LIS.

1 State of the art and preliminary work

Wetting is a ubiquitous phenomenon occurring when a liquid deposited on a substrate spreads out.[1-3] It is of fundamental importance and relevant for many applications that range from adhesion to heat transfer.[4-8] The properties of substrates, including both morphology and chemical composition, play an important role in the wetting behavior.[9] While the wetting behavior of droplets on various solid substrates has been intensively investigated, the study of droplets on liquid-based substrates is a recent field that is still in the ascendant.[10] A lot of understanding developed from the interaction with solid substrates cannot be directly applied to predict the wetting behavior of droplets on liquid-based substrates due to the intrinsically dynamic nature of these substrates and the strong liquid-liquid coupling effect between the droplet and the substrate.[11]

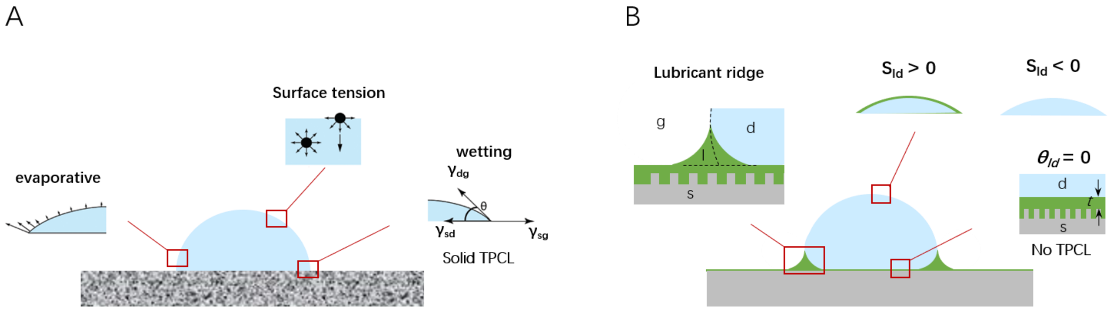

Figure 1. Wetting configuration of a droplet on a solid substrate (A) or on a lubricant infused surface (B). The labels *g*, *d*, *l,* and *s* mean air (gas phase), droplet (liquid phase), lubricant (oil phase) and the solid substrate.

The most representative system of liquid-based substrates is known as lubricant-impregnated surfaces or slippery liquid-infused porous surfaces. These lubricant infused surfaces (LIS) are constructed by infusing rough or porous materials with lyophilic oils (Fig. 1B). The design of these surfaces, specifically the choice of a rough solid and a lubricant for a given impinging fluid based on energetic considerations, is well-understood and their significance is recently recognized through developments reported independently by Quéré and Aizenberg et al. in 2011.[12,13] Afterwards, Varanasi et al theoretically analyzed the fundamental features of the wetting configurations on LIS under different conditions[14] while Wang et al. developed a model from the wetting criteria to predict the unknown surface energies for LIS design.[15] As shown in Fig. 1, the typical wetting configuration of a liquid drop on LIS is different from that on solid surfaces. On solids, there is always droplet liquid-solid-air three phase contact line (TPCL) at the droplet's base whereas on LIS, depending on the surface energies of the solid, lubricant, and drop, several typical configurations can be observed.[14] From the 12 thermodynamically stable states of a liquid droplet placed on a LIS,[14] here we make reference only to the slippery state which requires a lubricant-solid substrate contact angle of zero (θ_{ls}= 0), i.e. the existence of a stable oil interlayer between the droplet and solid substrate, therefore, no solid TPCL. This condition is the main difference between the wetting of a drop on a solid substrate and on a LIS. It is generally accepted that the presence of the mobile interlayer leads to the various advantageous wetting properties of LIS, such as the low contact angle hysteresis, high resistance to high pressure and humidity, self-cleaning, drag reduction, anti-icing/fouling etc.[12,16-24] The thickness of this liquid interlayer is very important for stability and bio-repellency while the viscosity of the lubricant has a stronger effect on the mobility and the drop retraction rate during bouncing.[25] For example, when increasing lubricant viscosity, the splashing threshold appears at a larger Weber number.[26] However, studying the liquid interlayer by experimental methods is challenging, not only due to its dynamic nature but also due to its small thickness. As a result, the experimental data on this interlayer is scarce. Another major difference between the wetting of a drop on solids and on LIS is the lubricant ridge formed at the lubricant–droplet–gas three-phase contact line in LIS system due to capillary action. Previous studies suggest that the presence of the lubricant ridge introduce competing dissipation mechanisms acting on a drop as it moves across LIS.[14,27] Keiser et al. first highlighted in 2017 that viscous dissipation may occur predominantly in the drop or in the lubricant depending on the ratio between the drop and lubricant viscosities.[28] Semprebon and Tress et al. theoretically studied this ridge in detail based on a model where a lubricant–droplet–gas three-phase contact line exist (no cloaking layer).[27] They used numerical methods to solve the Young-Laplace equation for different ridge geometries and showed that the apparent contact angle induced by the ridge is not uniquely defined by material parameters, but also has a dependence on the size of the lubricant ridge.[29] Moreover, the apparent contact angle and the shape of the ridge plays an important role in the droplet mobility: for large apparent angles, contact line pinning dominates and drops with more wetting lubricants move faster, while for small apparent angles, viscous friction in the lubricant ridge dominates and therefore, the magnitude of the viscous dissipation is determined by the shape of the lubricant ridge, and as such, drops in LIS with less wetting lubricants move faster.[27,29] In addition to the mobility of droplets on LIS, the presence of the lubricant ridge also induces the formation of a stable droplet interface bilayer when two droplets collide on LIS.[30] This occurs when the lubricant ridges from neighboring drops overlap and spontaneously merge together to minimize their surface energies; this results in a lubricant film squeezed upward forming a barrier between the colliding droplets. However, this phenomenon was studied without considering the influence of the volume of the lubricant ridge to the criteria of droplet coalescence and obtained conclusion could fail in the presence of a big lubricant ridge. When the extension of the applicability of physical models to different conditions is still under continuous development, experimental methods that can provide tunable variations in-situ to verify these hypothesis/models are still at a lack. Yet another important feature particular of a drop on resting on a LIS is the emergence of a cloaking layer.[14] The criterion for cloaking is given by the spreading coefficient, $S_{ld(g)} = \gamma_{dg} - \gamma_{dl} - \gamma_{lg}$, where γ is the interfacial tension between the two phases designated by subscripts d droplet, l lubricant, and g gas. Thus, $S_{ow(a)} > 0$ implies that the lubricant will cloak the droplet whereas $S_{ld(g)} < 0$ implies otherwise. Currently, no systematic study has been conducted to describe the contribution of the cloaking layer to the wetting and relative behaviors of droplets on the LIS. This is most likely due to the difficulty of quantitative measurement of the cloaking layer.[31] It has been observed from experiments that when this film is relatively thin, it cannot prevent the droplet coalescence, but it could delay the evaporation rate of the droplet and change the contact line.[32]

The establishment of the understanding of the wetting and moving of droplets on LIS basically depends on the methods used for observation and characterization. By means of confocal fluorescence microscopy which can provide space- and time-resolved microscopic information about the shape of the lubricant interface, Butt and Vollmer et al. were able to establish the presence of the lubricant cloaking layer on a droplet, as well as the stability of lubricant trapped within micropores and between microstructures.[31] This method also helped them to observe the evolution of the shape of the lubricant/droplet and droplet/gas interfaces and to solve the extended Young–Laplace equations for the drop/gas, drop/lubricant, and lubricant/gas interfaces numerically. However, it is difficult to conclusively confirm the presence of a stable intercalated lubricant film that separates the liquid droplet from the raised features of the solid substrate because of the relatively low resolution of confocal fluorescence microscopy (in the range of μm). To address this issue, Daniel et al made use of thin-film interference effect instead to probe the static and dynamical states of the intercalated film at a resolution down to a few nanometers and confirmed the existence of the continuous lubricating thin film (25 nm in their case) in a static state.[33] They also built a customized cantilever force sensor with sub-micronewton accuracy and measured the dissipative force acting on a moving droplet.[34] With these novel measuring methods, they disclosed that the dissipative force is independent of the initial lubricant film thickness and the size of the lubricant ridge (in the system without any TPCL). They also claimed in an open manuscript how the lubricant thickness changes dynamically with speed and can be deduced analogous to the classical Landau-Levich-Derjaguin problem by balancing the pressure gradient and viscous stress at the edge of the lubricant ridge.[35] However, their substrates do not allow for in-situ regulation of the lubricant thickness and the shape of lubricant ridge to further verify their hypothesis. In addition to the advanced technology, novel substrates with controllable physical parameters are also very important to develop the understanding of the wetting behavior on LIS. Stone et al have designed a microfluidic flow cell constructed with a patterned surface containing well-defined groove for exploring the mechanism of shear-driven loss of fluid.[36] Based on the novel substrate, they established the geometric surface parameters governing fluid retention.[37] Wong et al. develop slippery rough substrates which allow them to precisely calculate the apparent contact angle and evaluate the theoretical limitation of Wenzel models.[38] In their study, only slippery Wenzel state was investigated; the transition from Cassie to Wenzel state cannot be studied due to the lack of reliable regulation of the transition.

Despite this progress, the wetting-relative behaviors of droplets on LIS, including (de)wetting, moving, evaporation, and coalescence, are far from being fully understood and further progress requires not only the development of physical models which can consider more parameters but also the advancement of experimental systems and methods that can tune these parameters in-situ for the verification of various hypothesis. Although a number of LIS systems have been developed,[21,22,39-46] these are basically application-driven and normally could not provide systematic data to support the development of fundamental understanding. On the other hand, the approaches currently used for tuning the parameters do not allow in-situ manipulation and therefore, a series of samples are required for testing a single parameter which could increase the uncertainty in the observations. For example, to verify the criterion of wetting configuration, various material systems using lubricants with different surface tension were prepared.[15] Although these samples provided useful information to verify static models, the dynamic aspects such as the evolution of wetting configuration of droplets on LIS and the growth of the lubricant ridge of a moving droplet (it is the main source of lubricant depletion, i.e. the lubricant that a moving droplet collects as it sweeps across a lubricant-infused surface) have not been fully tackled. In some cases, the wetting behavior can only be studied in a dynamic state, for example, droplet collision and the transition from Cassie to Wenzel state.

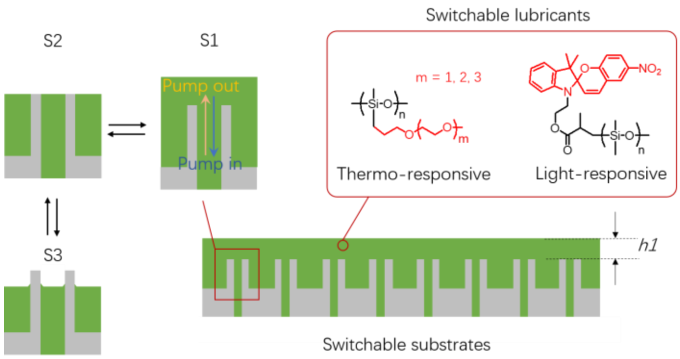

Figure 2. Schematic model of designed systems with switchable substrates and lubricants.

In this project, experimental methods are proposed to develop fundamental understanding of these wetting-relative behaviors of simple droplets on LIS, with specific attention to in-situ regulation of both chemical and physical parameters. With the concept schematically represented in Figure 2, switchable substrates and lubricants will be developed to create LIS systems in which the surface tension of lubricant, the thickness of lubricant overlayer, and the morphology of the substrate can be tuned to modify the wetting of a droplet. The substrates consist of surfaces with well-defined hollow structures. The channels within the substrates allow the pumping in/out of the oil to control the thickness of the lubricant layer (*h1*) and thus the switching between the surface morphologies: lubricant-covered, flat, and rough states (S1, S2, and S3, respectively in Fig. 2). These substrates enable the controlled transition between different wetting configurations, for example, from Cassie to slippery Wenzel state. This renders a useful tool for further understanding of basic aspects. Moreover, supramolecular materials that can self-adapt their surface morphology (see detail in *Preliminary work*) will also be used to prepare the substrate for studying dynamic apparent contact angle. On the other hand, in addition to normal lubricants, we will prepare and use lubricants whose surface tension and viscosity can be tuned under external stimuli. This will enable the in-situ variation of a larger range of parameters. For example, thermo-responsive lubricants that show temperature-dependent surface tension can be used to recreate/simulate the surface-energy-based criteria for LIS design. In comparison to thermo-responsive lubricants which normally vary in a time-resolution way, light-responsive lubricants can alter their surface tension in a space-resolution mode and this can allow the verification of many hypotheses, for example, the dependency of droplet's coalescence rate to the area of droplet interface bilayers. Moreover, the chromophore (spiropyran) appended on the end of lubricant molecules is fluorescent in the open-ring state,[47] which will allow us to image the cloaking layer. Note that high-content fluorophore in the lubricant can significantly increase the emission intensity for imaging. With the use of switchable lubricants in these switchable substrate systems, we can provide a full-spectrum of variations to verify various fundamental hypothesis and models. To realize the proposed concept, both knowledge in LIS and skills in structure fabrication and organic synthesis are required.

Preliminary work

My group has experience on 1) dynamic/switchable LIS, 2) synthesis of stimuli-responsive oil, and 3) fabrication of meso-structural surfaces with hollow pillar array.

1) For the past years, my group has worked on LIS with specific attention to dynamic substrates and switchable lubricants.[48-55] We have developed a strategy to create self-regulated LIS that allow the constant formation of a thin liquid overlayer that can prolong the surface slipperiness.[49] These systems are constituted by a silicone-based supramolecular gel (uPDMS) in which silicone lubricants are stored as droplets (Figure 3A). With these systems, we confirmed that in the case of the spreading factor $S = \gamma_{dg} - (\gamma_{lg} + \gamma_{dl}) > 0$, the surface tension can stabilize the formation of a liquid overlayer on the substrate. The thickness of the liquid film on the gel surface is determined by the disjoining pressure which creates a driving force to restore the original thickness when the liquid layer is depleted by moving droplets on the surface. It leads to continual replenishment of the consumed oil maintaining the thin liquid top layer of about 200 nm (Figure 3B). We further studied how the difference in surface tension induce lubricant transport in the film (Figure 3C).[50] Moreover, by applying external impact, we disclosed the contribution of the coupling interaction between the object (solid or liquid) on the surface (Figure 3D).[53] Recently, we found that the contact angle of a water droplet on these slippery surface is dynamically oscillated, during the evaporation of the droplet, because of the deformation of the substrates (Figure 3E). The experience and skill on LIS are highly relevant to the current project and will help us to conduct proposed tasks smoothly. The materials developed will also be used in this project to prepare adaptive surfaces.

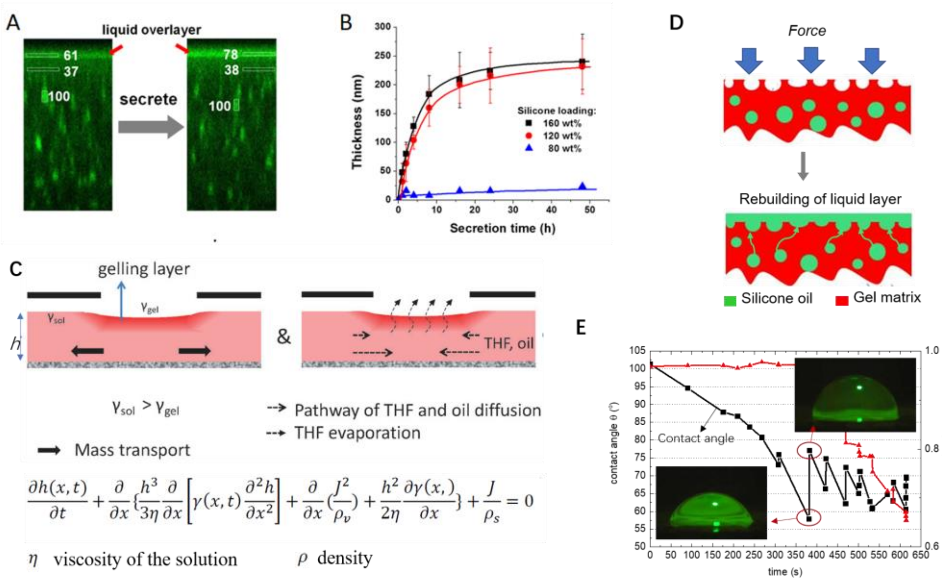

Figure 3. Self-regulated LIS. Lubricant release from droplets to surface (A) and its release kinetics (B). (C) The surface-tension-gradient induced Marangoni flow in the LIS film. (D) Mechano-induced replenishment of lubricant on a rough surface. (E) Wetting-induced release of lubricant from the substrate.

2) We have also worked on the synthesis of switchable lubricants. By grafting triethylene oxide as side chains to silicone oil, we have synthesized a class of thermo-responsive oils with lower critical solution temperatures (LCST) in water (Figure 4A).[52,56,57] The oils can be infused into polypropylene membranes to form thermo-responsive LIS. At a temperature higher than the LCST of the infused oils, the LIS is water-repellent while at the temperature lower than the LCST, the oils are miscible with water and therefore the droplet would diffuse into the oil phase and completely wet the solid surfaces (Figure 4B). We estimated the interaction parameter of water/oil mixture under different temperatures by both experimental and simulation (dissipative particle dynamics) methods, and confirmed that the parameter shows a sharp change when the temperature varies around the LCST, accompanied with a change of > 9.1 mN m^{-1} in surface tension. This switchable LIS system allowed us to study the failing and recover process of LIS with water droplets on the top and to disclose that water can penetrate into the hydrophobic substrate and completely retract out with a coast (Figure 4C). These oils will be applied as thermo-responsive lubricants in this project for switching the spreading factor. The synthetic method will also be applied to prepare other thermo-responsive lubricants. In addition to the synthesis of thermo-responsive lubricants, we also have experience in the synthesis of spiropyran-based materials.[47] These experiences will help us in preparation of light-responsive lubricants.

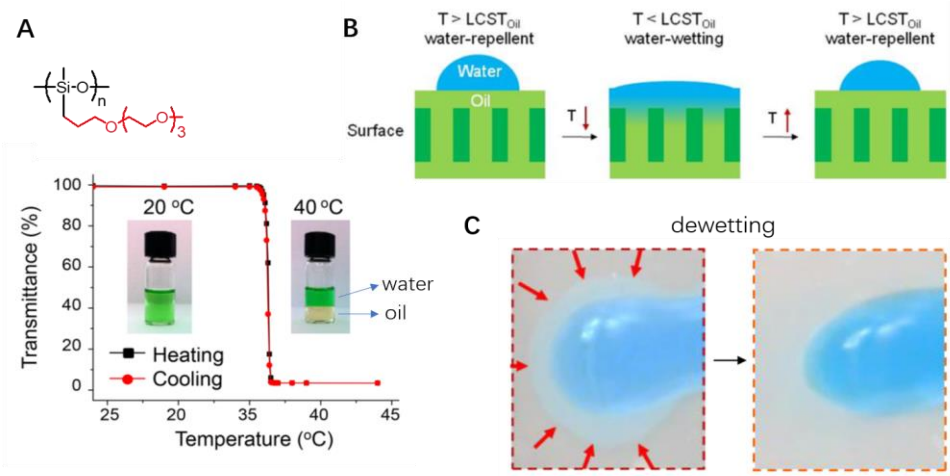

Figure 4. Thermo-responsive LIS. (A) Silicone-based oils with LCST in water; (B) Schematic of switchable wetting on the thermo-responsive LIS; (C) Retraction of a droplet on thermo-responsive LIS at 40 °C.

3) We have some experience with the fabrication of switchable structural surfaces. Recently, we have developed a class of meso-structural surfaces with hollow pillar array. A type of three-part molds was designed and fabricated as the templates of soft lithography. With these templates, we have prepared meso-structural surfaces that allow the pumping in/out liquid on demand. This method is suitable for various material systems, such as a magnetic-responsive elastomer that can be used to control surface morphology. Moreover, through the design of the middle part of the templates, a mushroom structure can be introduced to the hollow pillar. The integration of these structured surfaces with traditional microfluidic system enables precise manipulation of the liquid droplets on the top of the pillar. In our current research, the pillars have a high aspect ratio of L/D= 5 (length/diameter) and big diameter (500-800 µm) for individual and independent control of pillars. Although the systems developed in my group can't be used directly in this project because of the large size of the pillar, the knowledge and skill learned from these experiences will definitely support the current proposal. Note that the hollow pillar in tens of micrometer will allow us to fabricate the structural surface with simple templates made from photolithography combined with other microfabrication processes such as etching. Moreover, for this application, the aspect ratio of the pillar can be lower. These requirements will decrease the difficulty in the preparation of the structural surface.

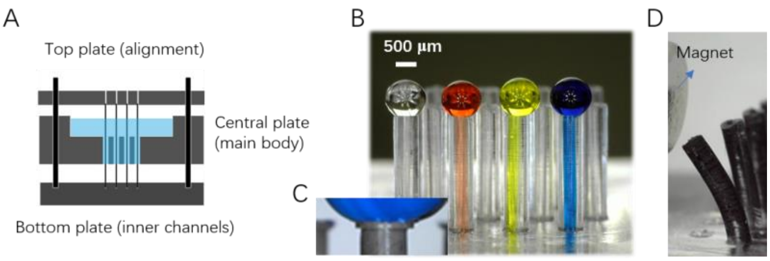

Figure 5. Meso-structural surfaces with hollow pillar array: (A) template; (B) A sample with droplets pumped out from bottom microfluidics; (C) Mushroom structure on the pillar; (D) Magnetic responsiveness of hollow pillars.

1.1 Project-related publications

1.1.1 Articles published by outlets with scientific quality assurance, book publications, and works accepted for publication but not yet published.

1) Zhao, H.; Sun, Q.; Deng, X.; **Cui, J.**, Earthworm-inspired rough polymer coatings with self-replenishing lubrication for adaptive friction-reduction and antifouling surfaces. *Adv. Mater.* **2018**, *30*, 1802141;
2) Oh, I.; Keplinger, C.; **Cui, J.**; Chen, J.; Whitesides, G. M.; Aizenberg, J.; Hu, Y. Dynamically Actuated Liquid-Infused Poroelastic Film with Precise Control over Droplet Dynamics. *Adv. Funct. Mater.* **2018**, *28,* 1802632;
3) Schlaich, C.; Fan, Y.; Dey, P.; **Cui, J.**; Wei, Q.; Haag, R.; Deng, X., Universal, Surfactant -Free Preparation of Hydrogel Beads on Superamphiphobic and Slippery Surfaces. *Adv. Mater. Interface* **2018**, *5*, 1701536;
4) Zheng, Y.; Liu, X.; Xu, J.; Zhao, H.; Xiong, X.; Hou, X.; **Cui J.**, Thermoresponsive Mobile Interfaces with Switchable Wettability, Optical Properties, and Penetrability. *ACS applied materials & interfaces* **2017**, *9*, 35483-35491;
5) Liu, P.; Zhang, H.; He, W.; Li, H.; Jiang, J.; Liu, M.; Sun, H.; He, M.; **Cui, J.**; Jiang, L.; Yao, X. Development of “Liquid-like” Copolymer Nanocoatings for Reactive Oil-Repellent Surface. *ACS Nano* **2017,** *11*, 2248-2256;
6) Zhao, H.; Xu, J.; Prieto-López, L. O.; Jing, G.; Deng, X.; **Cui, J.**, Controlling the localization of liquid droplets in polymer matrices by evaporative lithography. *Angew. Chem. Int. Ed.* **2016,** *55*, 10681-10685;
7) **Cui, J.**; Daniel, D.; Grinthal, A.; Lin, K.; Aizenberg, J., Dynamic polymer systems with self-regulated secretion for the control of surface properties and material healing. *Nat. Mater.* **2015**, *14*, 790-795;
8) **Cui, J.**; Drotlef, D.-M.; Larraza, I.; Fernandez-Blazquez, J. P.; Boesel, L. F.; Ohm, C.; Mezger, M.; Zentel, R.; del Campo, A., Bioinspired actuated adhesive patterns of liquid crystalline elastomers. *Adv. Mater.* **2012**, *24*, 4601-4604.

1.1.2 Other publications

No relevant other publications

1.1.3 Patents

1.1.3.1 Pending

Li, L.; Aizenberg, J.; **Cui, J.**; Weaver, J. C. Bio-inspired tough glass hybrid materials comprising polymeric adhesives. WO2016196040A1, 2016

1.1.3.2 Issued

Aizenberg, J.; Aizenberg, M.; **Cui, J.**; Dunn, S.; Hatton, B.; Howell, C.; Kim, P.; Wong, T. S.; Yao, X. Slippery self-lubricating polymer surfaces. *2014*, WO2014012080A1.

2 Objectives and work program

2.1 Anticipated total duration of the project

The intended duration of the project: 3 Years

2.2 Objectives

This proposal aims to provide a deeper understanding of the physical phenomena of droplets on LIS, from an experimental perspective. It will depend on the development of switchable LIS systems that allow for in-situ modulation of both morphologic and physicochemical parameters. With the regulation of the physical and chemical aspects of the lubricant layer and substrate, we seek to verify proposed wetting configurations and to develop the understanding of the transition between these states on LIS. The specific objectives are:

- Developing switchable lubricant infused surfaces (switchable LIS) that allow changing lubricant thickness, surface morphology, and the physicochemical properties of lubricants including composition, viscosity, and surface tension.

- Verifying the criteria for different wetting configurations on LIS proposed in previous studies by varying the wetting configurations in-situ.

- Disclosing the transformation of droplet profile from Cassie to slippery Wenzel state; verifying the transition criteria; developing fundamental understanding on slippery Wenzel state, including the criteria for the droplet sliding and the consumption of lubricant when droplets move.

- Developing reliable methods to regulate the size and shape of lubricant ridge; verifying the energy dissipation mechanism of lubricant ridge.

- Developing fundamental understanding on the cloaking layer, including verifying the criteria of its formation and identifying the relationship between its thickness and the properties of lubricants (surface tension); understanding the dynamic nature of the cloaking layer and its contribution to the evaporation of a droplet.

- Understanding the depletion of lubricant as droplets move on LIS under fixed conditions (i.e. replenishing lubricant to retain the thickness of the lubricant layer) and evaluating its contribution to the stability and longevity of LIS.

- Identifying the factors controlling the droplet bilayer interface of two collided droplets on LIS and developing approaches to manipulate the coalescence.

2.3 Work program incl. proposed research methods

The development of the switchable substrates and the synthesis of functional lubricants will be conducted together. The rest of the activities will be carried out parallel based on the development of these to fulfill the aims of this proposal on time.

Task 1: Design and fabrication of structural surface with hollow pillar array

The main characteristic of these substrates is the ability to control the thickness of the lubricant layer on demand and at the same time the possibility to modify the properties of the lubricant *in situ*. Two kinds of switchable substrates will be prepared. The first one will be done by the integration of a membrane (e.g. porous polypropylene member) with a polydimethylsiloxane (PDMS) supporting layer containing a microchannel network which will act as the means for lubricant release and withdrawal. The topography (pore size and morphology) of the membrane will provide the structure to 'fix' the lubricant layer on the surface while the subsurface structure in the supporting layer will provide the mechanism to control the thickness of lubricant layer within the range between few to hundreds of microns. The integration of the membrane and PDMS supporting layer will be done by an easy 'inking' process where uncrosslinked PDMS will be used as the adhesive to bond both parts.[46] The process is illustrated in Fig. 6A; a thin film of PDMS is spin coated on a glass substrate which represents the 'ink reservoir', then the supporting layer structure will be dipped in this reservoir while still uncrosslinked and then pressed against the polymeric membrane. A part of the uncrosslinked PDMS will wick on the porous structure and will render the anchoring points once fully crosslinked. This kind of switchable substrates is easy to prepare and has small porous size (depending on the commercial membranes, from 100 nm to 10 μm). The second type of substrate will be fabricated using soft lithography with a special mold fabricated using deep reaction ion-etching by the Bosch process in which multiple alternating plasma etching (SF_6) and deposit of passivation layer (C_4F_8 deposition) steps will allow the carving of the silicon wafer with structures of few tens of μm in diameter a relatively high aspect ratio required for the structure rendering the internal channel of the pillars. This fabrication process is illustrated in Fig. 6b (the thickness of the PDMS precursor will be controlled by spin-coating speech). This kind of switchable substrates seek to provide an ordered structure with similar switchable characteristics as the first kind of substrates but with a surface with regular features and big porous size (tens to hundreds of μm). They will allow the application of analytical models to predict or simulate the behavior of the interfaces. More than simple PDMS, supramolecular gel uPDMS will also be applied to prepare the substrates. Because of the dynamic nature of uPDMS, we expect that the substrate will deform after a droplet is placed on the top, which provides a platform for studying the dynamic contact angle during droplet's moving.

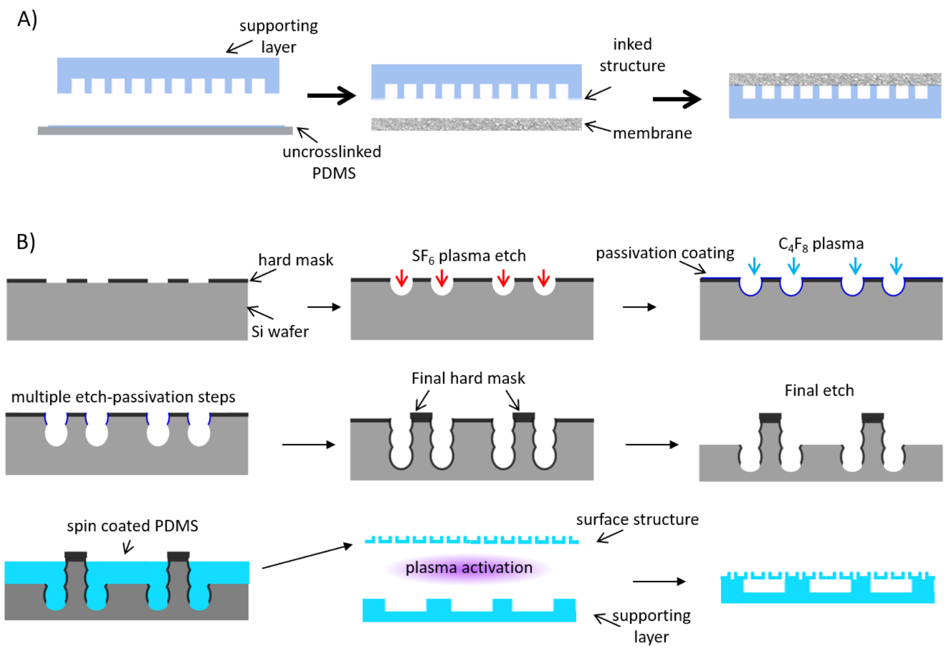

Figure 6. Fabrication process of A) first type switchablesubstrates and B) fabrication process of mold for second type of switchable substrates. substrates

Task 2: Synthesis and characterization of switchable lubricants

Two kinds of responsive lubricants are designed, i.e. thermo- and light-responsive lubricants, as shown in Figure 7. We have prepared a kind of thermo-responsive lubricants with LCST in water[52] and the same synthetic method will be applied to prepare thermo-responsive lubricants consisting of olig(ethyl glycol) as side chains and methylsiloxane as the backbone. The polymer degree (n) will be varied to change the viscosity of the lubricant while the length of the side chain (m) will be used to tune the lubricant−droplet interaction parameters (surface tension). Light-responsive lubricants contain a spiropyran terminal group which can be switched between hydrophobic close-ring form and hydrophilic open-ring form by UV and visible lights, respectively. This alternation will change not only the surface tension but also the viscosity of lubricants. They can be prepared via the coupling reaction of OH-functional spiropyran and carboxyl-terminal silicone oil. Note that these switchable lubricants can be either employed directly or diluted in normal silicone lubricants to tune the switching ranges in surface tension and viscosity. The viscosity and surface tension of the lubricants and their mixtures will be characterized under dynamic conditions, i.e. varying temperature and light irradiation. The viscosity of the lubricants under different conditions (different temperatures and irradiation states) can be obtained from a rheometer equipped with a thermo-control table or a transparent table allow for in-situ liquid-irradiation (Discovery HR-3 hybrid rheometer). Pendant drop method (on a goniometer equipped with a thermo-control table) will be employed to evaluate the surface tensions in both air and water. The change in molecular structure of light-responsive lubricants can be confirmed by its color and the photo-switching kinetics will be obtained by collecting the absorption spectra by UV spectroscopy under different irradiation dose. With these measurements, we will establish the quantitative relationships between temperature/irradiation dose and surface tension/viscosity. These data will allow us to estimate the change in spreading factor S under different conditions and thus to predict the wetting configurations.

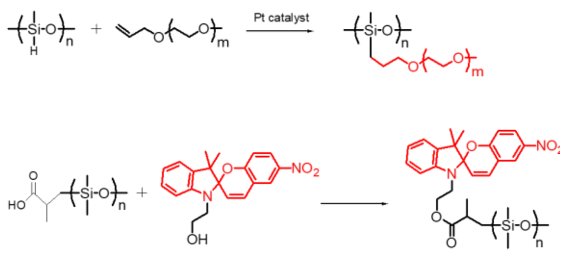

Figure 7. Synthesis of switchable lubricants

Task 3: Characterization of the switchability of LIS with water droplets

An initial characterization of the switchable substrates and lubricants will be done separately at first. A normal lubricant, i.e. not modified, e.g. commercial mineral oil, will be injected into the substrates through the channels embedded on the supporting layer. The thickness of the lubricant layer on the top will be measured by ellipsometry (< 1 μm) or laser scanning confocal microscopy (> 1 μm). Note that laser scanning confocal microscopy (LSCM) has been applied to directly observe the droplet on LIS in the previous study.[31] This well-established method will be employed in this project, i.e., dying the water droplet and lubricant with fluorescent markers emitting lights with different wavelengths. Both commercial dyes (e.g. Bestoil Red 4B for mineral oil and Alexa Fluor 488 for water) and the silicone-based dyes (red dye for silicone oil) developed in our group will be used to get the image. The initial calibration will establish the relationship between differential pressure or volume injected (controlled by syringe pump KD Scientific Legato 101 or Elveflow pressure controller OBI MK3) and the thickness of different lubricants in agreement to their viscosity and density. In the case that uPDMS is used to prepare a kind of self-adaptive substrates, we will monitor the deformation of the substrate and also the change in apparent contact angle in the presence of a droplet. The information will help to disclose the jump of contact angle during the evaporation of a droplet on the top of surface. On the other hand, the switchable lubricant will be infused into a porous substrate, e.g. polypropylene membranes, to study the responsiveness of the lubricants. Water contact and sliding angle will be used to estimate the change in surface tension. The change in viscosity will be estimated from the sliding rate. The information obtained from these experiments in addition to those obtained in a free liquid state in *Task 2* will allow us to understand the contribution of the porous substrates to these properties. Finally, the switchable lubricants will be injected into the switchable substrate for testing the orthogonality of tuning lubricant thickness and lubricant properties (viscosity and surface tension). On one hand, the flexibility of controlling the parameters such as the thickness of lubricant layer and the viscosity and surface tension of lubricants, will be tested and the knowledge developed will be used to guide the following tasks. On the other hand, we will also verify the surface-energy-based criteria of stable LIS. Briefly, one droplet (e.g. water, ionic liquid, and glycol) will be placed on the switchable LIS. The lubricant composition will be continuously changed by pumping in one new lubricant and pump out original one at the same time. By selecting the lubricants, we can easily alternate the contact angle (θ_{ls} > 0 or <0) and spreading factor (S_{ld} >0 or <0) in situ to verify the criteria. In addition, responsive lubricants will also be applied to test the criteria by in-situ changing their surface tension (might alternate θ_{ls} and S_{ld}) or miscible state.

Task 4: Controlling the transitions between wetting states

Figure 8 shows the strategy we will follow to study the wetting state of a water droplet placed on top of the switchable substrate impregnated with normal lubricants. First, a water droplet will be gently placed on the substrate partially infused with lubricant, i.e. surface asperities exposed, and a Cassie state is expected as that suggested in previous studies. If the infusing lubricant has larger spreading coefficient on the solid ($S_{ls} \equiv \gamma_{sg} - \gamma_{sl} - \gamma_{lg}$) than droplet ($S_{ds} \equiv \gamma_{sg} - \gamma_{sd} - \gamma_{dg}$), one can make the lubricant-solid contact angle θ_{ls} zero by increasing the level of lubricant enough to cover the surface and form an interlayer between water drop and substrate, thus no more contact between solid and drop exist. In this condition and when the drop is only partially covered by the lubricant, a liquid TPCL will be formed between gas, lubricant, and droplet (water). In the extreme covering case, the lubricant will fully cover the drop forming a cloaking layer. By pumping lubricant into the substrate, we will remove the entrapped air between the droplet and substrate and switch from the Cassie state to normal slippery state. In this state, a lubricant ridge is expected to form around the drop. We will monitor the change in the lubricant ridge and the apparent contact angle with increasing the thickness of the lubricant layer, by using both setups for laser-induced fluorescence, i.e. confocal microscopy and perpendicular imaging. Both fluids, water and lubricant, will be dyed for this measurement. When depleting the substrate from the lubricant, by suction of the lubricant inwards, we expect the formation of Wenzel state. We will study the contact angle and mobility of the droplet in this state. The control of lubricant thickness (checked by LSCM) will allow us to evaluate the relationship between lubricant thickness and sliding angle and the pinning of the droplet in Wenzel state (h_3 in Figure 8). Note that slippery rough surfaces allow for more precise measurement of apparent contact angles (and then quantitative validation of the Wenzel wetting models as well as theoretical contact angle predictions and the fundamental limits of these theoretical models) due to their low contact angle hysteresis. Moreover, roughness (R) is the main parameter introduced in many models to describe the wetting behavior of droplets on surfaces but it has rarely been varied in-situ by an experimental method to validate their limitation. We will demonstrate the flexibility of our system to this purpose by verifying the Kang-Jacobi wetting model[58] that is derived on the basis of work of adhesion, conservation equations, and surface energy minimization to relate the apparent contact angle to the surface roughness (the R will be controlled by h_3 in our system).

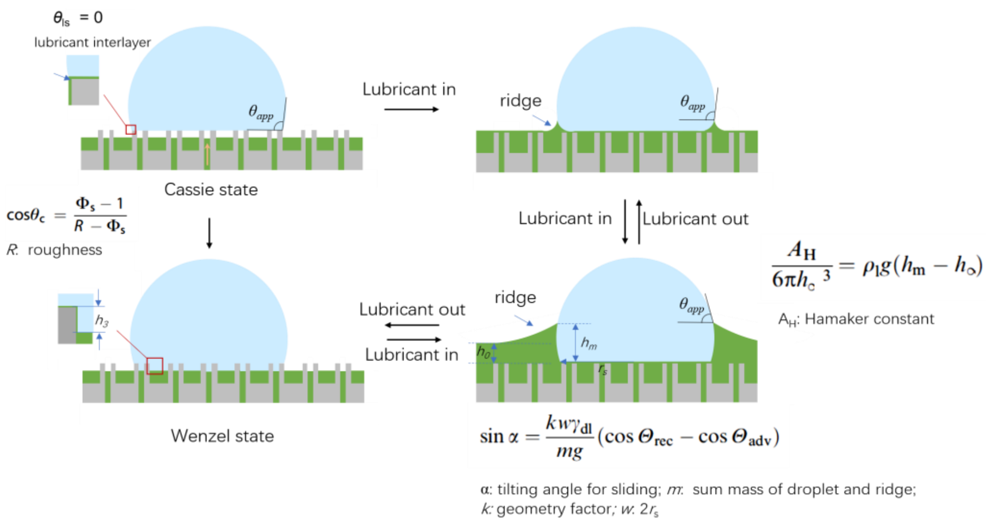

Figure 8. Droplet on switchable LIS with controllable lubricant thickness.

Task 5: Evaluation of the contribution of lubricant thickness to the wetting behavior of droplets on LIS

With the system described in Figure 8, we will vary the lubricant thickness to study 1) shape changes of the ridge and the droplet, 2) droplet mobility on LIS, and 3) depletion of lubricant and longevity of LIS. For the first sub-task, LSCM will be used to describe the shapes of both the droplet and lubricant. The results will help us to confirm the models developed by Vollmer and Butt et al. (the equations described in Figure 8). After the calibration of the shape change, we will study the mobility of a water droplet on the LIS by varying the tilting angles (α) on the LIS with different thickness of lubricant (changing the mass of lubricant ridge). It is suggested that the formation of lubricant ridge decreases the sliding angle of the drop due to an addition of effective mass and the lower interfacial tension. The information obtained from the droplet mobility will allow us to quantitatively evaluate the contribution of the lubricant ridge. Moreover, we will also calculate the depletion of the lubricant by monitoring the oil consumption (based on the amount of lubricant in the syringe connected with the substrate retaining a constant thickness). The consumption rate will be estimated at different lubricant thickness. We expect that the depletion mainly depends on the volume of the lubricant ridge. Quantitative calculation can disclose their relationship and help to estimate the longevity of LIS with fixed lubricant content.

Task 6: Imaging and analysis of cloaking layer

It has been suggested that the equilibrium thickness of the cloaking layer can be calculated by equating the capillary pressure in the cloaking film caused by the drop curvature, and the disjoining pressure. The film thickness is:[31]

$$B = \left(\frac{A_H R}{12\pi\gamma_{lg}}\right)^{\frac{1}{3}}$$

where B is the thickness of cloaking layer, A_H is the Hamaker constant, R is the radius of the droplet. The film is normally very thin (tens nanometers). Recently, confocal microscopy has been successfully used[31] to partially observe the lubricant cloaking layer. Basic aspects regarding this cloaking layer such as the thickness and extension on the droplet are still inconclusive. We aim to further analyze these aspects of the cloaking layer using confocal microscopy in addition to other laser-induced fluorescence configuration such as illumination and observation from a perspective perpendicular to the substrate. This configuration is sketched in Fig, 9. The experimental setup includes laser sheet illumination formed with a set of lenses and filters arranged along the optical path between the laser and the drop resting on the lubricated surface and a set of filters placed between the drop and the camera. In this configuration, the laser and camera are perpendicular to each other and perpendicular to the plane of the substrate. A combination of fluorescent dyes, so to mention PDI-conjugated silicone oil (soluble in the lubricants and not in water) and Alexa Fluor 488 (soluble in water but not in the lubricants), will be employed for these measurements. We will use both normal lubricants with different surface tension (e.g. decanol, mineral oil, silicone oil, and FC70) and responsive lubricants to study the cloaking layer. Normal lubricant will be used to verify the relationship between the thickness of lubricant and surface tension. Note that although the thin cloaking layer is difficult to observe directly, the emission from the

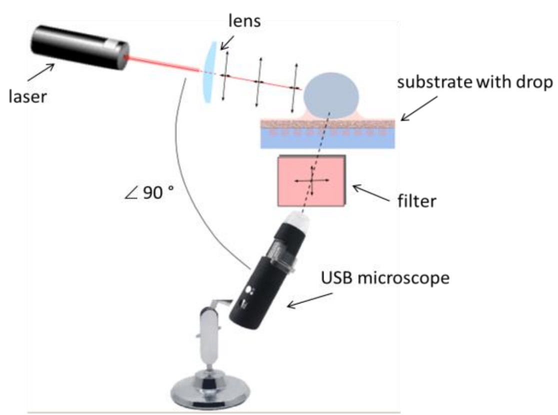

Figure 9. Laser induced fluorescence setup with illumination and observation plane perpendicular to the substrate

cloaking layer can be used to estimate the relative thickness of the layer. When the thermo-responsive lubricants are used, we will change the temperature and monitor the change of the cloaking layer. In the case that the change in lubricant surface tension can alternate the spreading factor from $S_{ld} < 0$ to $S_{ld} > 0$, we will observe the formation of cloaking layer. In addition to the change in surface tension, we will also change the thickness of lubricant layer, which will decrease the radius of the area explore to air and thus change the thickness of cloaking layer too. Furthermore, the light-responsive lubricants will also be employed in this study because of its high fluorophore-content. By increasing the fluorophore content, we will be able to increase the emission intensity of the cloaking layer to quantitatively estimate of the thickness of the layer.

Task 7: Regulation of droplet evaporation on LIS

Switchable lubricants will be infused into the switchable substrates for this study. Although no systemic study has been conducted to discuss the contribution of cloaking layer on the evaporation rate of droplets on LIS, previous results have suggested that the droplets on LIS could show slower evaporation rate than those on other substrates.[32] We attribute this to the preventing effect of lubricant ridge and cloaking oil layer. It is known that on a solid substrate with a thermo-conductivity higher than air, liquid in the droplet would evaporate faster at the TPCL.[59] On LIS, the thick lubricant ridge at the contact line on the bottom edge of the drop should prevent the liquid evaporation (thus the evaporative area is reduced, Figure 10). On the other hand, the thin cloaking layer at the apex of the drop should also decrease the evaporation rate since the molecules need to diffuse through the thin lubricant layer. To study the evaporation rate, we will place water droplets with same size on the LIS with different lubricant thickness and then evaluate the contribution of lubricant ridge and cloaking layer separately. On one hand, we will fix the height of lubricant ridge and vary the lubricant surface tension (this will change the apparent contact angle and thickness of cloaking layer) and viscosity (the penetration rate of water molecules) to study the evaporation rate. On the other hand, we will fix lubricant and change the height of the lubricant ridge to monitor the evaporation processes. Tracking particles, either fluorescent or silica/carbon particles, will be added into the droplet to trace the evaporation model inside of the droplet. The particles will be tracked with the aid of a high-speed camera (Optronics CamRecord CR3000x2, Germany) and image analysis by the inbuilt software TimeViewer in combination with Image J. These experiments will allow us to compare the evaporation on LIS to that occurring on normal substrates which are well studied.

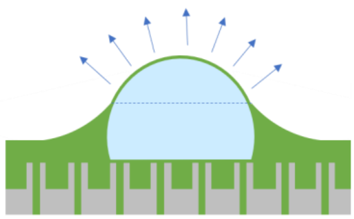

Figure 10. Evaporation of a droplet on LIS

Task 8: Regulation of droplet coalescence on LIS

It has been suggested by Boreyko et al that the thin cloaking layer does not prevent the coalescence of colliding droplets.[30] Therefore, when two water droplets came into contact at droplet-air (without cloaking interlayer) on a LIS, they coalesced relatively fast. However, if the lubricant ridges around the drops merge together before the contact between droplets occurs, they will form a droplet interface bilayer (DIB), and in this circumstance, the coalescence will depend on the surface

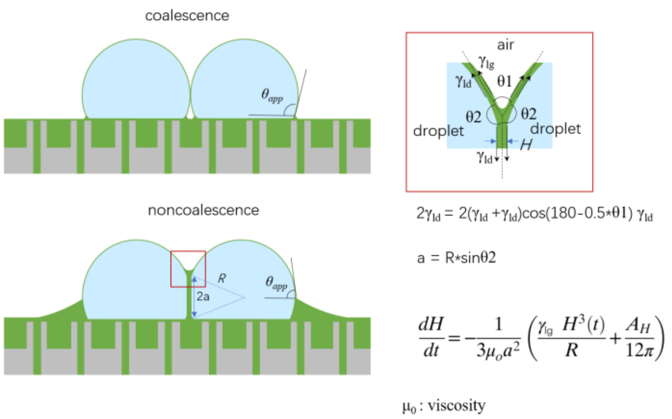

Figure 11. Coalescence of droplets on LIS

tension and the area of the DIB. We herein expect that the apparent contact angle on the ridge (shown in Figure 11) will be the key factor to control the coalescence state: increasing the thickness of lubricant (or the size of lubricant ridge) will decrease the apparent contact angle. It was suggested that an apparent contact angle lower than $90\ ^{o}$ would allow the formation of DIB thus preventing the 'immediate' coalescence. However, in the case with a relatively large lubricant ridge, the apparent contact angle continuously changes when two droplets collide, because of lubricant emerging. Therefore, we expect a critical apparent contact angle of $> 90\ ^{o}C$ in the presence of a relative big ridge. We will collaborate with Prof. Butt and Dr. Berger in MPIP on studying the dynamic apparent contact angle during the moving of the droplet. We will apply the home-built Drop Adhesion Force Instrument (DAFI) developed by them to manipulate the colliding of the droplets. DAFI will allow us to control the colliding velocity. We will snap the colliding process of two droplets with an initial apparent contact angle of $> 90\ ^{o}C$ under different thicknesses of lubricant layer (thus different volume of lubricant ridge) by a high-speech camera. The results will allow us to deliver the criteria for droplet coalescence on LIS and understand the relationship between the apparent contact angle and the moving velocity. On the other hand, the drainage of the oil film is primarily due to the Laplace pressure and long-range intermolecular forces acting across the film and the thinning rate will depend on the area of DIB (*a* in Figure 11) and the viscosity of the lubricant. When a switchable lubricant (i.e. light-responsive lubricant) is employed in the system, we will be able to simulate the presence of surfactant since the hydrophilic state of the lubricant can act as a surfactant to stabilize the droplet. On the other hand, in the case of lubricants which only change their surface tension and viscosity, we will be able to vary the contact angle ($\theta 2$ in Figure 11) and thus also change the coalescent rate. With these studies, we will develop the guiding rule for the manipulation of droplet coalescence on LIS.

Planned time schedule

Task		Year 1		Year 2		Year 3	
1	*Design and fabrication of structural surface with hollow pillar array*						
2	*Synthesis and characterization of switchable lubricants*						
3	*Characterization of the switchability of LIS with water droplets*						
4	*Controlling the transitions between wetting states*						
5	*Evaluation of the contribution of lubricant thickness to the wetting behavior of droplets on LIS*						
6	*Imaging and analysis of cloaking layer*						
7	*Regulation of droplet evaporation on LIS*						
8	*Regulation of droplet coalescence on LIS*						

2.4 Data handling

Concluding data will be published in patent or/and research article mode.

2.5 Other information

No relevant

2.6 Descriptions of proposed investigations involving experiments on humans, human materials or animals

No relevant

2.7 Information on scientific and financial involvement of international cooperation partners

No relevant

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4 Requested modules/funds

4.1 Basic Module

4.1.1 Funding for Staff

1 Ph.D. students for 3 years (starting in September 2019)

One Ph.D. student in material science will conduct the fabrication of the substrate, the synthesis and characterization of responsive lubricants, and investigate the wetting behaviors of droplets on switchable LIS containing responsive lubricants. His/her work will be supported by other group members (experts in organic synthesis or dynamic LIS). He/she will be paid at a level of 66% according to TV-L EG 13 (west).

Because of a lot of repeat measurements, financial assistance for summer-students in material science from German Universities (HiWi Stelle) is required. The student will help in repeated measurements in contact angle and surface tension etc.

1 student for 3 months each year, 600 €/month

4.1.2 Direct Project Costs

4.1.2.1 Equipment up to €10,000, Software and Consumables

Consumables:

Chemical reagents, precursors, solvents, chemical laboratory consumables 8000 €

Consumables for structural characterization (Deuterium solvents for NMR, polymer standard for GPC, outward elemental analysis etc.) 500 €

Photomask, access to clean room and photolithography, consumable in clean room

12000 €

Total consumable: 20500 €

4.1.2.2 Travel Expenses

JC requests travel funds for the Ph.D. student to visit collaborated groups, one international and one natural conference on surface chemistry or material science during the Ph.D. research. **3000 €**

4.1.2.3 Expenses for Laboratory Animals

This project does not relate to any animal experiment

4.1.2.4 Other Costs

No relevant

4.1.2.5 Project-related publication expenses

Color illustrations and publication in Open Access journals **2000 €**

5 Project requirements

5.1 Employment status information

Jiaxi Cui, Dr.
Independent junior research group leader at INM - Leibniz Institut for New Materials, Campus D2 2, 66123 Saarbrücken, Germany

Temporal position until March 2020

5.2 First-time proposal data

No.

5.3 Composition of the project group

List only those individuals who will work on the project but will not be paid out of the project funds. State each person's name, academic title, employment status, and type of funding.

Three researchers (**JC,** a PhD student, and a HiWi student) will involve in this project.

JC will work in this project. He will design and supervise the project, analyze the results.

The Ph.D. student will conduct the experiments and analyze the results.

The HiWi student will assist the Ph.D. student in material preparation and measurements.

5.4 Cooperation with other researchers

5.4.1 Researchers with whom you have agreed to cooperate on this project

We will cooperate with Prof. Hans-Jürgen Butt and Dr. Rüdiger Berger from the Max Planck Institute for Polymer Research (MPIP). We send a student to the MPIP group where he will learn to use the Drop Adhesion Force Instrument (DAFI. This instrument will then be used for experiments to study the collision of droplets resting on a different lucubration layer. Videos captured with a high-speed camera should provide details of droplet coalescence. In particular, we aim to understand the role of the apparent contact angle and the lubrication ridge for droplet coalescence.

We will also cooperate with Prof. Doris Vollemer in MPIP. Prof. Doris Voller is preparing gel-based slippery system. We plan to exchange samples to investigate the consequences of switching on the deformation of the wetting ridge of moving drops.

5.4.2 Researchers with whom you have collaborated scientifically within the past three years

JC is the core member of *Leibniz Research Cluster* and works closely with Dr. Vito Valiante in Leibniz Institute for Natural Product Research and Infection Biology HKI, Jun.-Prof. Martin Weissenborn in Leibniz Institute for Plant Biochemistry, Dr. Julian Thiele in Leibniz Institute of Polymer Research Dresden, and Dr. Erik Freier in Leibniz Institute for Analytical Sciences, for developing cell-free biosynthesis methodology of active compounds. In this project, **JC** is charging the fabrication of meso-structural surface with hollow pillar array that can deliver liquid to the surface and manipulate the moving of liquid droplets (a technique will be used in this project). In the field of lubricant-infused surface (LIS), **JC** cooperates actively with Prof. Joanna Aizenberg at Harvard and Prof. Yuhang Hu at University of Illinois Urbana-Champaign on dynamic LIS system, with Prof. Zuankai Wang at City University of Hong Kong and and Prof. Guanyin Jing at Northwest University (China) on the physics mechanisms behind the wetting behaviors of droplets on LIS, with Prof. Deng at University of Electronic Science and Technology of China on the application of dynamic LIS. **JC** also works with Prof. Gerhard Wenz at Saarland University in the synthesis of responsive polymers. In INM, **JC** has long cooperation activity with the team of Prof. Aránzazu del Campo on switchable surfaces on studying the interface interaction. These collaborating topics are highly relevant to this proposed project. The knowledge and experience learned from the cooperation will contribute to this project which will be completely conducted in INM.

5.5 Scientific equipment

Larger instruments including laser scanning confocal microscopy, ellipsometry, syringe pump, rheometer, goniometer, laser-induced fluorescence setup, NMR, MS, UV absorption and fluorescence spectrometers etc. mentioned in the proposal are available in INM; cleaning room and photolithography instrument are outward available in Saarland University. The workshop department in INM has the facility to manufacture various molds and home-designed small devices.

5.6 Project-relevant cooperation with commercial enterprises

No relevant

5.7 Project-relevant participation in commercial enterprises

No relevant

6 Additional information

No relevant