FABRICATION OF SLIPPERY LIQUID-INFUSED POROUS SURFACES USING
LAYER-BY-LAYER ASSEMBLY: TOWARDS MULTIFUNCTIONAL SURFACES
AND FACILE FABRICATION PROCESSES

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ABSTRACT

Slippery liquid-infused porous surfaces (SLIPS) are bioinspired omniphobic surfaces that use a very thin layer of lubricant locked within the surface micro/nano structure to repel a variety of liquids. These surfaces could have a potential impact on a wide range of industries, including healthcare, food packaging, and automobile. In this master thesis, SLIPS are fabricated by the state-of-the-art layer-by-layer (LbL) assembly of polyelectrolytes. LbL assembly is a simple and fast thin film fabrication technique which is performed by sequential immersion of substrates into polyelectrolyte solutions. The studies presented here describe an effort to utilize LbL assembled polyelectrolyte multilayers (PEMs) to create multifunctional SLIPS and on developing novel LbL system in organic solvent to achieve a facile, fast, and scalable fabrication of SLIPS. A novel gel-infused slippery surface with a gelator containing lubricant is demonstrated. This surface exhibits temperature-dependent and gelator concentration-dependent water drop sliding properties. In some cases, this means temperature dependent transition from water pinning to water sliding surfaces. The robustness of the lubricant layer against wash, a big concern for SLIPS, is proved to be enhanced by the addition of gelator, and an optimal 0.5 weight % concentration of gelator in mineral oil is found to best preserve the surface properties under a moderate shear flow. In addition to making multifunctional SLIPS, a tremendous effort has been focused on developing novel fabrication methods for making SLIPS. LbL assembly of branched polyethylenimine and Nafion is performed with methanol as the solvent. Hierarchically rough and superhydrophobic surface is obtained directly without
further modification on various substrates. The surface properties are shown to highly depend on the LbL assembly parameters, including deposition cycles, dipping time, rinsing time, and drying time between baths. The polyelectrolyte multilayers obtained with this method is infused with Krytox®100 to form SLIPS surfaces, which show excellent omniphobic, antifouling, self-cleaning, flexible, and optical properties. The new method not only simplifies the fabrication of SLIPS surfaces, but also provides useful insight for making LBL films with specific morphologies.
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CHAPTER I

INTRODUCTION

1.1 The Layer-by-layer Assembly

Polymeric materials have significantly changed our daily life in all aspects. Their application can be found in hydrogels,[1–4] batteries,[5–9] and absorbent.[10–12] In this master thesis, the use of polyelectrolytes, polymers bearing charges, are utilized to fabricate thin films using the layer-by-layer assembly.

The layer-by-layer (LbL) assembly is a nanoscale thin film fabrication technique which can be used to make a wide range of functional surfaces.[13–15] The traditional LbL assembly utilizes the electrostatic interaction between oppositely charged polyelectrolytes to form polyelectrolyte multilayers (PEMs). Other intermolecular interactions, including hydrogen bonding,[16,17] coordination bonds,[18,19] and covalent bonds[20,21] can also be utilized to perform LbL assembly. A variety of materials, such as nanoparticles,[22,23] proteins,[24,25] or DNA[26,27] can be used in LbL assembly. The LbL assembly is famous for its simplicity and versatility. The LbL assembly is carried out by sequentially immersing the substrate into polyelectrolyte solutions, and then repeating the process for a desired number of cycles. This means LbL can be applied to any substrates accessible to solution, no matter the shape and geometry. A good example is the development of microcapsules
via LbL assembly using microparticles as templates.\cite{28,29} In addition to traditional dip coating, the LbL can also be done with spin-assisted coating\cite{30,31} and spraying coating\cite{32} for much faster fabrication.

Most of the LbL assembly are performed with polyelectrolytes in aqueous solutions, with water rinsing steps in-between. Although the LbL assembly is directed by intermolecular interactions such as interaction and hydrogen bonding, the process is driven by entropy gain with release of counterions and hydration water molecules.\cite{33} Polyelectrolytes can be divided into two categories, namely strong polyelectrolytes and weak polyelectrolytes. The strong polyelectrolytes are constantly charged polymer when dissolved in water, independent on the pH value of the solution. Functional groups, such as quaternary ammonium group and sulfonate group, are commonly found in strong polyelectrolytes. The charge density of weak polyelectrolytes, on the other hand, is dependent on the pH of the solution when dissolved in water. Amine group and acid group are commonly found in weak polyelectrolytes. For strong polyelectrolytes, the assembly equilibrium can be tailored by ionic strength, due to screen effect. For weak polyelectrolytes, the assembly equilibrium can be tailored by the pH.

![Scheme 1. Young's model.](image)
LbL assembly is widely considered as an environmentally-friendly and low-cost technique. It is a great surface modification technique for achieving various functionalities on a wide spectrum of materials. In this master thesis, this technique is specifically used to create surfaces with special wettability.

1.2 Surface Wettability

1.2.1 The Young’s model

Wetting of surfaces is an important phenomenon and has been long studied. The wettability of a surface by a liquid reflects the affinity between the liquid and the surface. Water, the most abundant liquid in the world, is mostly used as the test liquid when it comes to studying surface wettability. Contact angle (CA) or static contact angle measurement is gold-standard for assessing surface wettability. Conventionally, CA is the angle between liquid/vapor interface and liquid/solid interface at equilibrium. However, the vapor phase can also be replaced by a second liquid phase immiscible with the testing liquid.

The CA of a liquid on a flat solid surface depends on the surface tension between three phases as shown in Scheme 1. The CA can be numerically described by Young’s equation:

\[ \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \]  

(1)

where \(\gamma_{SV}\), \(\gamma_{SL}\), and \(\gamma_{LV}\) represent surface tensions between solid-vapor, solid-liquid, and liquid-vapor phases, respectively. As seen from the Young’s equation, with fixed testing
liquid, and vapor phase, the CA reflects the surface tension of the solid. When the CA is measured with water droplets in air, and the CA is greater than 90°, the surface is considered hydrophobic. If the CA is smaller than 90°, the surface is hydrophilic. For a flat surface, the water CA is solely determined by the chemical composition of the solid. However, the hydrophobicity of the surface can be increased by roughness.[34]

1.2.2 Wenzel wetting model

When rough surfaces are wetted by liquids, two separate regimes can take place, namely, Wenzel state and Cassie-Baxter state. Under Wenzel wetting regime, the rough surface is completely wetted by the liquid (Scheme 2). The apparent CA of a droplet on a rough surface with Wenzel regime can be described by the following equation:

$$\cos \theta^* = r \cos \theta$$

(2)

where \( r \) is the roughness factor of the surface defined as the ratio between actual surface area and projected area, \( \theta^* \) is the apparent CA under Wenzel state, and \( \theta \) is the CA defined in Young’s equation if the droplet were sitting on the flat surface made of the same material. The roughness factor \( r \) is always greater than 1 for rough solids, and is equal to 1 only when the solid is perfectly flat. For hydrophobic solids, \( \theta > 90^\circ \), \( \cos \theta^* < \cos \theta < 0 \), and
therefore $\theta^* \geq \theta$. This means hydrophobic material can increase its hydrophobicity by increasing surface roughness. On the contrary, a hydrophilic solid would exhibit increasing hydrophilicity with roughness.

1.2.3 Cassie-Baxter wetting model

When roughness continues to increase with hydrophobic materials, the wetting regime again changed to the so-called Cassie-Baxter model (Scheme 3). Different than the Wenzel model, where liquid conform to the rough solid structure, liquid droplets sit partially on the solid and partially on the air pockets trapped within the rough structure. This results in the famous superhydrophobic surfaces, where the CAs are larger than 150°. Assuming flat liquid-vapor interfaces for air pockets, the CA under Cassie-Baxter model can be calculated by

$$\cos \theta^* = -1 + (\cos \theta + 1)\phi_s$$

where $\theta^*$ is the apparent CA under Cassie-Baxter model, $\theta$ is the CA defined in Young’s equation on the flat surface, and $\phi_s$ is the fraction of the wetted surface. Because the CA on air is 180° according to Young’s equation, and the droplets sit partially on air and partial on air, the Cassie-Baxter model results in very large contact angles. With $\theta$ close to 110°

Scheme 3. Cassie-Baxter wetting model with CA of $\theta^*$. 

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and $0.05 < \phi_s < 0.1$, the apparent CAs between $160^\circ$ and $170^\circ$ are obtained.\cite{34} The Cassie-Baxter wetting model often requires special surface structure, such as hierarchical roughness and re-entrant structure to stable air trapping.

The Cassie-Baxter model not only predicts large CA it also results in small CA hysteresis and sliding/rolling off angles. Thanks to the large fraction of air at the liquid-vapor interface, liquid droplets experience very small drag force when moving along the solid surface. This dewetting property provide many natural surfaces with special functions. One of the most famous superhydrophobic and self-cleaning surfaces developed by nature is the lotus leaf (LL)\cite{35}. The conventional LL mimic self-cleaning and superhydrophobic surfaces are identified with their re-entrant hierarchical micro/nano structure\cite{36–38}. The surface morphology enables the Cassie-Baxter wetting model. As a result, the water droplets can roll off form the surface extremely readily and can wash away any dirt and dust along their way.

As powerful as are the superhydrophobic surfaces, they surfer from some serious weaknesses. A major pitfall with this type of surfaces is their instability, especially under high pressure\cite{39}. The hydrophobicity of LL type surfaces depends on the existence of the air pockets embedded with the surface structure. Once the air pockets get squeezed out and replaced by liquid, the surface dewetting property is impaired\cite{40–43}. This intrinsic drawback of LL mimic superhydrophobic surfaces prevents them from being used in some extreme environment, such as under deep water.
1.3 Slippery Liquid-Infused Porous Surfaces (SLIPS)

1.3.1 A bio-inspired surface

Inspired by the *Nepenthes* pitcher plants, Aizenberg et al.\textsuperscript{[44]} and Quéré et al.\textsuperscript{[45]} fabricated the SLIPS, which shows extremely low sliding off angle and sliding angle hysteresis for both water and liquids with low surface tension\textsuperscript{[46–50]}. Different than the LL type superhydrophobic surfaces, SLIPS exploit a layer of impregnated lubricant in place of air pockets found in LL mimics to achieve water/liquid repellency\textsuperscript{[44,45,50,51]} (Scheme 4). One can think of this strategy as replacing the compressible gas layer that lies between a lotus leaf like surface and the drops it repels with a non-compressible liquid layer. For such a system to work, the infused lubricant has to be immiscible with the liquids to be repelled, and the underlying structured surface must be preferentially more wettable by the lubricant.
This same mechanism is used by the *Nepenthes* pitcher plants to create slippery surfaces that helps them to capture insects. The microscale rough structure, shown in Figure 1, of the peristome surface of *Nepenthes* pitcher plants can be completely wetted by either nectar secreted by the plant or water harvested from rain or moist. A uniform liquid film can thus form at the surface serving as a lubricant layer. Infused lubricant, the peristome surface becomes super slippery for insects that land on the surface to climb upwards against it. With the help of this lubricating mechanism, the pitcher plants manage to catch insects for necessary nutrition supply. The invention of SLIPS demonstrated that this lubricating mechanism can also be used to prevent wetting and staining of surfaces by liquids other than the lubricant. In addition to being repellent to a wide range of liquids, the SLIPS also possess superb anti-ice, anti-frosting, anti-biofouling, self-healing properties, and condensation promoting properties. With specially integrated reservoirs, the SLIPS can have replenishing lubricant supply to counteract the loss of lubricant and achieve long term service.
1.3.2 SLIPS criteria

Liquid droplet mobility on SLIPS has been previously studied by Varanasi and coworkers.\cite{51} When a water droplet is placed on top of SLIPS, three distinct wetting regimes can take place. The first one is called impaled regime, where the infused lubricant is replaced by the water (Scheme 5a). In the emerged/impregnated regime, the solid structure is impregnated with lubricant, but top of the solid structure is emerged and makes direct contact with water droplets (Scheme 5b). The third wetting regime is called the encapsulated regime, where the solid structure is encapsulated by the lubricant, so the water droplet sits completely on a thin film of lubricating liquid and there is no direct contact between solid and water (Scheme 5c). The encapsulated regime ensures the water droplets to slide freely on the surface, whereas the impaled regime pins water droplets. For emerged regime, water droplets mobility depends highly on the solid texture. To achieve the encapsulated regime, the lubricant spreading coefficient on solid under water $S_{os(w)}$ has to be equal or larger than 0.\cite{51} The spreading coefficient is calculated by

$$S_{os(w)} = \gamma_{sw} - \gamma_{os} - \gamma_{ow}$$

where $\gamma_{ij}$ is the interfacial tension between $i$ phase and $j$ phase, and $s$, $w$, and $o$ stand for solid, water, and lubricating oil, respectively. The spreading factor depends only on the
chemical properties of solid material and lubricant, but not on surface texture. This means for a solid-lubricant pair that results in a positive spreading coefficient, a slippery surface can be obtain even with flat surface. This is the physical basis of some of the recently developed flat slippery surfaces.\[61,62\]

For the emerged mode to be stable, the following condition has to be satisfied. \([51]\)

\[-\gamma_{cw} \frac{(r - 1)}{(r - \phi)} < S_{os(w)} < 0\]  
(5)

On the other hand, if the opposite is true, that is

\[-\gamma_{cw} \frac{(r - 1)}{(r - \phi)} > S_{os(w)}\]  
(6)

the impaled mode will be more stable. Note that the boundary between the impaled and the emerged regimes is only defined by the surface texture, namely \(r\) and \(\phi\).

The chemical properties of lubricant and the porous solid are the most important factors to achieve slippery surface, because a good much of chemsitry for the solid and lubricant would ensure the encapsulated regime. However, such match of chemistry is not always available for specific applications and could restrict the type of the material for fabricating the SLIPS. Therefore, most SLIPS achieve slipperiness with emerged regime. This means the solid surface must poccess the right surface structure, so that Equation 5 is satisfied. As a result, a tremendous amount of effort was spent on developing novel fabrication methods to create the porous solid for making SLIPS.
CHAPTER II
GEL-INFUSED SURFACE WITH ENHANCED LONGEVITY AND THERMALLY CONTROLLABLE SLIDING PROPERTIES

2.1 Introduction

Self-cleaning and omniphobic surfaces that are resistant to many kinds of staining have the potential to make a great impact in various consumer and industrial applications.\cite{39,44,46} Surfaces of complex geometries such as lotus leaf mimics\cite{35,63} and those with re-entrant micro and nanostructures can have these properties,\cite{34,64,65} but are not very tolerant to damage or wear.\cite{66} If the complex geometry is damaged or if the surface becomes fouled under conditions of extreme temperature, a loss of function can occur.\cite{39} Lotus-leaf type structures require that pockets of air exist between the water drops that are to be repelled and the majority of the substrate, meaning that pressure can compress the structure and remove those air pockets.\cite{41–43,45} A simpler approach to creating surface repellency is to modify surfaces with perfluorinated acids, which has been widely adopted in products such as food packaging to create water and oil repellency,\cite{67} but chemical modification of flat surfaces alone cannot create truly superhydrophobic or omniphobic surfaces.\cite{34} Additionally, recent safety concerns regarding environmental persistence and bioaccumulation of perfluorinated acids are making use of these materials less desirable.\cite{67,68} A recently proposed strategy to creating slippery, self-cleaning surfaces that
are also self-healing and better able to withstand extreme conditions is to infuse a liquid or lubricant into a porous structure, creating a solid surface with a thin, smooth liquid layer on top.\[44,45\] One can think of this strategy as replacing the compressible gas layer that lies between a lotus leaf like surface and the drops it repels with a non-compressible liquid layer. These so called “slippery surfaces” (also known as SLIPS for slippery liquid infused porous surface) have the additionally benefit that the geometry requirements are not as strict as that of a lotus leaf structure. Such surfaces can repel water as well as oily liquids which are immiscible with the infused lubricant. These surfaces have some degree of self-healing as the liquid phase can flow back into damaged areas, and due to the non-compressibility of the fluid are less easily damaged under pressure compared to lotus leaf type structures. In addition to being self-cleaning, liquid-infused surfaces have been demonstrated to be useful for delaying ice crystallization, improving condensation, heat transport, and also as being anti-fouling.\[53,55,56,58,59,61,69\] While a number of applications have been examined, the range of liquids that have been used for infusion has been relatively limited, mainly to fluorinated lubricants and silicone oil, and water has also been demonstrated for repellency of oils.

Although liquid infused surfaces have superior properties in some aspects, there are limitations as well. One possible improvement which would make the surface even more versatile would be to introduce stimuli-response properties to the surface. Aizenberg et al. have developed stress-responsive SLIPS which exhibit completely distinct wetting behavior under stretched and relaxed states.\[70\] However, this mechanical stimulus needs to be delivered through stretching which involves direct contact of the surface. In addition, this stress-responsive SLIPS requires the whole surface to be mechanically stretchable,
limiting generality. Jiang et al. have developed SLIPS with thermally switchable surface adhesion properties, using paraffin as the lubricant and crosslinked polydimethylsiloxane as the substrate.\cite{71} However, this method is only viable when the substrate can swell in the lubricant. Moreover, their surface can only switch directly from water pinning to sliding but fail to exhibit any gradual change in surface wetting properties nor to possess a range of sliding speeds.

The most common failure mechanism for SLIPS surfaces is the loss of lubricant over time.\cite{72} This surface achieves its properties by allowing the liquid to be repelled to flow along the surface with the infused lubricant, but the flow of lubricant can also be a critical limitation. For example, there can be drainage of the lubricating liquid under shear in some cases, as demonstrate by Stone et al.,\cite{72} although Aizenberg et al.\cite{47} have shown that under very low flow rates this is not necessarily an issue. Another factor that can also lead to loss of lubricant is the cloaking phenomenon described by Varanasi et al.\cite{51} based on relative affinities between the solid substrate, lubricant, and the water drop.

Presented here is a novel strategy for creating a composite infused surface.\cite{73} Specifically, a porous substrate is infused with heated mineral oil into which an organogelator has been dissolved. As the precursor solution cools to room temperature it becomes a gel that is less able to flow than a liquid lubricant. By taking advantage of the temperature dependent rheology of the infused material, we create surface properties that vary with temperature. The room temperature properties of this gel-infused surface are much different than those under elevated temperatures. The gel-infused surface has longer longevity with respect to being washed in water as compared to the oil infused surface as well. This new composite surface represents a broadening of the type of liquid infused
surfaces that are presented in the literature as well as another parameter with which to control surface properties.

2.2 Experimental Section

2.2.1 Material

12-Hydroxystearic acid (12-HSA, Cat No. H0308) was purchased from TCI Co., Ltd. Silica nanoparticles (SNP, LUDOX® AS-40, 40wt% in H2O, Cat No. 420840) and Poly (diallyldimethylammonium chloride) (PDAC, average Mw = 100,000-200,000, 20wt% in H2O, Cat No. 409014) were purchased from Sigma Aldrich. n-Octytriethoxysilane (OTS, Cat No. SI06715.0) was purchased from Gelest, Inc. Mineral oil (vacuum pump oil 19, Cat No. 54996-082), Sulfuric acid (Cat No. BDH3072-2.5LG), and hydrogen peroxide (35% w/w in H2O, Cat No. BDH7814-3) were purchased from VWR International. Deionized (DI) water used in all experiments was produced from a Milli-Q DQ-3 system (Millipore, Bedford, MA, U.S.A.) with resistivity of 18.2MΩ. All materials were used as received without further purification.

2.2.2 Fabrication of PDAC/SNP Multilayer Film

Glass slides (Cat No. 48382-171, VWR) and silicon wafers were immersed into freshly prepared acid piranha solutions (mixtures of 98% sulfuric acid and 35% hydrogen peroxide at v/v=7/3) for 4 hr at room temperature. The substrates were then rinsed with excess DI water to remove any residual piranha solution on the surface. The substrates were then treated with air plasma for 5 min to create negative charges on the substrate surface right before the layer-by-layer (LBL) assembly. The LBL assembly was performed
by a dip-coating robot, StratoSequence VI (nanoStrata Inc.). The substrates were first immersed into a bath of 0.1wt% PDAC solution for 10 min, followed by three baths of DI water (each with 1 min dipping time), and then they were immersed into 0.1wt% SNP colloidal suspension for 10 min, followed by another three DI water baths (each with 1 min dipping time). This cycle was repeated to create multilayer films with desired number of layers.

2.2.3 Removal of Organic Layer

To remove the polymer layer, the multilayer films were placed in a muffle furnace (Ney Vulcan 3-130). The temperature was increased from room temperature to 500°C at a rate of 10°C/min, held at 500°C for 3 hr, and cooled down to room temperature at 10°C/min.

2.2.4 Characterization of SNP film

Scanning electron microscopy (SEM) images were obtained using a JEOL-7401 field emission scanning electron microscope with an accelerating voltage of 5.0kV. The film thickness and void ratio were measured by a variable angle spectroscopic ellipsometer (VASE, M-2000 UV−visible−NIR [240−1700 nm] J. A. Woollam Co., Inc., Lincoln, NE, U.S.A.). To fit the ellipsometry data, a four-layer model consisting of a silicon substrate layer (Si Temp JAW, Temp Library, temperature 25 °C), a fixed Si-SiO2 interface layer (INTR JAW, thickness 1.0 nm), a thermal oxide layer (SiO2 JAW, thickness 0.8 nm), and a Cauchy layer (with thickness, A and B free fit parameters) or a EMA layer (with Material#1 being SiO2 and Material#2 being void) was employed in Complete EASE (J. A. Woollam, Co., Inc., Lincoln, NE, U.S.A.).
2.2.5 Chemical Vapor Deposition of OTS

Chemical vapor deposition (CVD) of OTS was performed after the calcination step. Four SNP films was first treated with air plasma for 10 min and then placed in a vacuum desiccator. A vial containing 20μL OTS was placed together with the SNP film in the vacuum desiccator. The CVD was carried out under reduced pressure for overnight.

2.2.6 Impregnating lubricant

Gel lubricant precursor solutions were prepared by completely mixing 12-HSA with mineral oil at 90°C. The melt lubricant was impregnated into the SNP film by dip-coating at 90°C and withdrawing speed of 5mm/min using a KSV NIMA small single vessel dip coater. After the substrates were completely withdrawn from the lubricant reservoir, they were allowed to cool down to room temperature in order for the lubricant to gel.

2.2.7 Contact angle measurement

All contact/sliding angle measurement was performed on VCA optima (AST products) equipped with a tilting stage at ambient condition. Static contact angle measurements were taken by slowly placing a 1.5μL DI water droplet onto the substrate surface and then using the VCA software to fit the outline of the droplet. Sliding angles were determined with a 10μL DI water droplet on tilting stage. Sliding angle is taken as the tilting angle at which the water droplet starts to slide. All measurements were repeated at five different spots on the substrate and averaged.
2.2.8 Sliding Speed measurement

Water droplet motion over these sample surface was treated as uniform linear motion, and the velocity was calculated by $v=s/t$. In all sliding speed tests, 10µL droplets were carefully placed onto the surface and allowed to slide down the surface. The sliding process was recorded by a SLR camera (Canon EOS SL1). Sliding distance and time were then determined by Movie Maker and ImageJ. The temperature of the incline was measured by a thermal image camera (Testo 870, Testo limited.) Each test was repeated for at least 3 times.

2.2.9 Lubricant stability test

The setup of the washing experiment is schematically shown in Fig. 6(a). Gel-infused surfaces (1cm×2cm) were positioned at approximately 45°. A syringe was used to deliver DI water dropwise onto the gel-infused surface (with no impacting velocity). The water flowrate was controlled by a syringe pump at 1ml/min. The gel-infused surface was moved from side to side during the washing process, so that the entire surface was uniformly washed. After the surface was washed by each 5ml water, the contact angle was recorded. The surface was then heated up to 80°C for sliding speed measurements. A total volume of 30ml water was used to wash each gel-infused surface.

2.2.10 Rheology measurement

Rheology measurements were conducted on a strain-controlled rotational rheometer (ARES G2, TA instruments) using a parallel plate geometry of 25mm diameter. Small amplitude oscillatory shear was used to investigate the frequency dependence of dynamic moduli at 20, 40, 60 and 80 °C. The frequency range was 0.0398-39.8 Hz, and the
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The strain amplitude was within the linear viscoelasticity range as determined from strain amplitude sweep by varying the strain, \( \gamma = 0.1-100\% \), at a frequency of \( \omega = 0.159 \text{ Hz} \).

2.3 Result and Discussion

2.3.1 Silica Nanoparticle (SNP) film characterization

The porous film used to construct the thermally responsive gel-infused surface in this study is the SNP film which was previously developed by Aizenberg et al.27 The fabrication process is schematically depicted in Scheme 6. A layer-by-layer (LBL) assembly of poly(diallyldimethylammonium chloride) (PDAC) and SNP is used to fabricate a multilayer film. The organic component is removed through heat treatment (500°C), and the resulting SNP film is 69% porous as shown by spectroscopic ellipsometry (Figure 2). The large void to solid ratio makes this substrate a good reservoir for infusing with lubricant. The SNP film surface is then modified with octyltriethoxysilane (OTS) via chemical vapor deposition (CVD) under reduced pressure. This silanization step renders the surface hydrophobic by reducing the surface energy with alkyl groups, increasing the
affinity between the surface and the lubricant. Finally, the film is infused with heated mineral oil containing the organogelator, which gels as the mixture cools down resulting in a gel-infused surface. The contact angle of the CVD treated SNP film is \(~130^\circ\) (Figure 3), and after infusing the surface with mineral oil/gel lubricant, the surface contact angles decrease to \(~90^\circ\) at room temperature with a slight decrease with increasing organogelator concentration, but only a few degrees. Determination of surface tension of the mineral oil and mineral oil infused with organogelator proved challenging. Pendant drop measurements made under ethanol give values of 3.25 mN/m for mineral oil in ethanol and 3.19 mN/m for mineral oil containing 0.25 wt% of the organogelator in ethanol. Higher
concentrations become too stiff to perform the measurement. After treating glass slides with an alkane silane it was possible to also spin coat thin films of the mineral oil or mineral oil with the different concentrations of the organogelator. A water drop was stable on none of these surfaces, spreading within seconds of being placed on the surface and displacing the lubricant in strong contrast with behavior observed on the slippery surfaces. This behavior was similar for all concentrations of the organogelator, including pure mineral oil, leading to the qualitative conclusion that the surface tension of the gelled mineral oil does not vary greatly with the addition of varying amounts of organogelator. Despite the fact that

Figure 3. Contact angle measurement of CVD modified SNP using a 2µL water droplet.

Figure 4. Photographs of gelled mineral oil containing 0.25%, 0.5%, and 1% 12-HSA at room temperature in tilted vials.
the organogels are slightly opaque in bulk (Figure 4), the gel-infused surfaces are highly transparent (Figure 5).

2.3.2 Thermally responsive surface properties

Mineral oil gelled with 12-hydroxystearic acid (12-HSA) is intrinsically thermally responsive as the rigidity of the gel varies with temperature. The gelation of the organogel is based on hydrogen bonding and crystallization of the 12-HSA. The phase transition temperature lies around 72°C, corresponding to the melting point of 12-HSA. Among the concentrations investigated in this study, a rigid organogel formed at room temperature when the concentration of 12-HSA was 1% or higher (Figure 4). The word “gel” used in this article is a loose descriptor for all gelator containing mineral oil.

In this work, sliding speeds of water droplets on surfaces tilted at a fixed 30° were used to evaluate the surface slipperiness. The actual roll off angle for all of these surfaces varied, and 30° was used as a constant for sake of comparison. The sliding speeds of water

![Figure 5. Photograph of 0.25%, 0.5%, 1%, and 2% gel-infused surfaces, showing good transparency optical properties.](image)
droplets on the gel-infused surface with various 12-HSA concentrations and under four different temperatures were measured (Figure 6a). The results show that water drops slide faster at higher temperature and on surfaces infused with lubricant containing less amounts of gelator. The sliding speeds on all gel-infused surface increase dramatically from 60°C to 80°C, consistent with the phase transition temperature of the organogel. In comparison, the sliding speed for mineral oil-infused surface (with no gelator) exhibits a large increase when heated from 20°C to 40°C and the increase rate declines from 40°C to 80°C. From a qualitative perspective, the temperature-driven change in surface sliding property is most prominent for the surface infused with most concentrated gel, as it switches from water pinning to sliding from 60°C to 80°C. For the other three concentrations (0.25%, 0.5%, and 1%) tested, the sliding speeds first increased gradually as the surfaces were heated from room temperature to 60°C and large increases were observed when the temperature reached 80°C, showing a wide range of controllable sliding speeds. This trend is also observed in surface contact angle measurements at different temperatures (Figure 6b). The

Figure 6. (a) Water droplets sliding speeds on 30° tilted lubricant infused surfaces with various concentration and under 20°C, 40°C, 60°C, and 80°C, and (b) water droplet contact angle under the same conditions.
water contact angles on gel-infused surfaces in general decrease as the temperature rises, and the decrease is most noticeable with the 2% gel-infused surface. This observation is consistent with the sliding speed measurements. Both sliding speed and contact angle measurements show that the surface properties of gel-infused surfaces can be thermally tailored. The reduction of surface tension of water on the slippery gel infused surfaces may indeed aid in the ability of the water drop to flow along the surface. By adding different amounts of gelator to the mineral oil, one can govern the range of controllable sliding speeds. In addition, the concentration of gelator also dictates whether there is a continuous change of sliding speed over a range of temperature or there is sudden switch of surface property from water pinning to sliding at some critical temperature.

Figure 7. Storage and loss moduli of (a) 0.25%, (b) 0.5%, (c) 1%, and (d) 2% organogel under various temperatures.
2.3.3 Temperature dependent rheological properties of organogel

The thermal response of the gel-infused surfaces stems from the change of the mobility of the infused lubricant under different temperatures. In order to validate this claim, rheological properties, namely storage moduli (\(G'\)) and loss moduli (\(G''\)), of the organogel with four concentrations of gelator were recorded under the same temperatures at which the sliding speed and contact angle were investigated. The results are summarized in Figure 7. For each concentration, both \(G'\) and \(G''\) of the organogel decrease with increasing temperature and decreasing 12-HSA concentration. Significant declines in moduli are observed at 80°C for organogels with all four concentrations as expected. The decrease in \(G'\) and \(G''\) at 80°C is most noticeable for the 2% gel (Figure 7d), consistent with the observation in sliding speed measurement. The rheological properties of the organogel show exactly the same trend as sliding speed and contact angle measurements under the same temperatures. This matches previously reported work whereby increasing the temperature of high molecular weight lubricant increases the sliding speed by decreasing the viscosity of the lubricant and increasing the ability to flow.

2.3.4 Stability of Thermal Response with Multiple Heating/Cooling Cycles

Any further development of these thermally responsive surfaces will require that the temperature dependent response is durable. To test the repeatability of the thermal response of the gel-infused surfaces, a 0.5% gel-infused was subject to a heating-cooling cycle between 80°C and 20°C for 8 times. The sliding speeds after each heating/cooling process were measured and result is summarized in Figure 8. The results indicate that the gel-infused surface was able to retain its thermal response throughout multiple heating and
cooling process. This stability of the surface upon repeated heating and cooling shows the potential of the surface to be utilized in long term applications.

2.3.5 Robustness of gel-infused surfaces

As previously mentioned, the lifetime and robustness of liquid-infused surfaces is a serious concern for their commercial implementation. The self-cleaning and non-wetting properties of SLIPS are realized by the fact that the lubricant can flow with water or oil droplets on the surface, but this also leads to the eventual loss of lubricant and surface properties. Gelled mineral oil is expected to act locally like a liquid, but will not flow away. As a first measure of lifetime, the surfaces were monitored over a week’s time and

![Figure 8. Water droplet sliding speed on 0.5% gel-infused surface heated and cooled between 80°C and 20° for 8 cycles.](image)
evaluated by weight and contact angle. That all of the surfaces do not lose mass over this
time to be best of our ability to quantify this (Figure 9) shows that the mineral oil and its
variants do not easily evaporate. Contact angles of the slippery surfaces also do not
appreicably change after one week for all compositions (Figure 10). The stability of
lubricant upon washing with water was also evaluated. Gel-infused surfaces were
positioned at 45° while water was delivered onto the surface with no impact speed by a

Figure 9. Relative mass change of lubricant of gel-infused surfaces over 8 days.

Figure 10. Contact angles on gel-infused surfaces with various gelator concentrations.
syringe. The experimental setup is schematically depicted Figure 11a. The surfaces were constantly moved from side to side to ensure an even wash over the whole surface. The contact angle and sliding angle evolutions as functions of washing volume are summarized in Figure 11b and c. As shown in Figure 11b, the contact angle of all surfaces increase as they are washed by DI-water. This increase in surface contact angle is caused by the loss of lubricant layer and the protruding of underlying porous structure, which has a lower surface energy than the lubricant. The extent of the increase in contact angle can thus be used to infer the amount of lubricant left on the surface. After the surfaces were washed with every 5ml aliquot of water, the contact angles were recorded. Then the surfaces were

Figure 11. (a) Schematic representation of wash experiment. (b) Surface contact angle and (c) sliding speed evolution on gel-infused surfaces being washed by DI-water.
heated up to 80°C and the sliding speeds on the washed surfaces were also measured to examine the surface slipperiness.

As shown in Figure 11b, the contact angles on pure mineral oil-infused surface and 0.25% gel-infused surfaces increase dramatically and reach a plateau right after being washed with 5ml water. It is because the mineral oil and 0.25% lubricant are highly mobile; the small amount of 12-HSA is not able to increase the robustness of the lubricant layer by a noticeable extent. As the concentration of 12-HSA increases to 0.5%, an obvious delay in the increase of contact angle is observed, indicating that upon being washed by same amount of water, substantially more lubricant is left on the 0.5% gel-infused surface than for the pure mineral oil and 0.25% cases. Based on the rheological measurements, it would be expected that the higher the 12-HSA concentration the more robust the surface will be. However, the 0.5% gel-infused surface proved to be the most robust among all the concentrations investigated in this study. As evidenced by the contact angle measurements, the 1% and 2% gel-infused surfaces are more robust than the pure oil-infused surface and 0.25% gel-infused surface, but less durable than 0.5% gel-infused surface. The sliding speed measurements made at 80°C (Figure 11c) also agree with the trend shown in contact angle evolution. One possible explanation for this phenomenon is that when the lubricant becomes too rigid, its ability to dissipate energy is compromised. As a result, the shear forces from the washing water are then more effective at abrading the 1% and 2% surfaces as compared to less concentrated gel surfaces. A second reason that the surface slippery properties of 1% and 2% gel-infused surfaces are more easily compromised than that of the 0.5% gel-infused surface is that the ability of highly gelled lubricant to flow back and restore the surface liquid repellent following damage and impact is much less than that of
the more liquid-like lubricant. As explained by Azienberg et al. the lubricant layer of SLIPS can flow towards the damaged area caused by abrasion and impact, providing the surface with self-healing properties. However, when the lubricant is a rigid organogel instead of flowing liquid, this self-healing property of SLIPS is likely to be compromised. It is expected that this method of gel infusion can be generalized so long as a uniform gel can be formed. For example, in this work samples were also made by adding 12-HSA to silicone oil, which partially phase separated and resulted in a surface with very non-uniform properties.

2.4 Conclusion

A novel method to fabricate a thermally responsive slippery gel-infused surface was demonstrated. The fabrication process includes a simple LBL assembly of PDAC and SNP, followed by high temperature calcination and vapor phase silanization. The slippery gel-infused surfaces developed in this study show excellent water repellency and optical transparency. The thermal response of the gel-infused surfaces is achieved by taking advantage of the temperature dependent rheological properties of the gelled mineral oil. The resulting gel-infused surface exhibits thermally controllable surface sliding properties, demonstrated by the change of water sliding speed at various temperatures. This fabrication method also enables control over the sliding speed and its thermal variation by simply varying the 12-HSA concentration. The addition of 12-HSA to mineral oil enhances the robustness of the lubricant layer compared to mineral oil alone, and an optimal concentration of 0.5% is identified to result in the most robust gel-infused surface in this study. The fabrication method developed here provides a brand-new way to generate
surfaces with thermally controllable surface wetting properties and this method could potentially be expanded to a wide range of lubricant/gelator system.
3.1 Introduction

Omniphobic surfaces that can resist the wetting of aqueous solutions, organic solvents, and biological fluids can benefit many industries. It has proven to be challenging to create surfaces that reliably resist liquids of arbitrary surface tension in a manner compatible with industrial fabrication methods. Superhydrophobic surfaces, such as lotus-leaf type surfaces have long been shown to resist wetting of water, and can be omniphobic if functionalized with fluorine.\cite{35,40,63} However, they suffer from their instability, especially under extreme working conditions, such as high temperature and pressure, as well as the difficulty to fabricate given the precise geometric requirements.\cite{41,42,66} Lotus-leaf type surfaces rely on the air pockets that are trapped in the micro/nano hierarchical structure to resist the wetting of liquids. This type of surface can lose its properties once the air is removed from those texture pockets and water wets the surface, such as under situations of high hydrostatic pressure.\cite{41,42,66} Recently, researchers have taken inspiration from the \textit{Nepenthes} pitcher plant, which uses a surface with a microscale rough structure to anchor a layer of water or nectar that then forms an extremely slippery surface for the
capture of insects.[52] By mimicking the pitcher plant, Aizenberg et al developed an alternative to superhydrophobic surface and named it slippery liquid-infused porous surface (SLIPS).[44] SLIPS utilize micro/nano porous solid to lock a film of lubricant which repels any other immiscible fluids.[45] The mobility of the lubricant allows liquids drops on the surface to easily slide off from that surface. The incompressible lubricant also gives SLIPS robustness that is lacked in other types of superhydrophobic surfaces. In addition, SLIPS can self-repair against mechanical damage, as the lubricating fluid can flow into and replenish voids caused by physical scratches or abrasion.

SLIPS type surfaces have been shown to have excellent omniphobic,[46,47] anti-icing,[53,54] anti-frosting,[55] antifouling,[49,60,69,74] and improved condensation[58] properties. Recently, smart SLIPS that exhibit distinct wettability under stimuli of mechanical stress[70] and temperature[71,73] were developed. Fundamental studies on SLIPS wettability and failure mechanisms have also been carefully conducted.[51,72] Most of the effort, however, has been spent on developing novel methods to fabricate SLIPS. Initially, Aizenberg et al. utilized periodically ordered epoxy-resin-based nanostructured surface and Teflon nanofibrous membrane as the solid matrix for SLIPS.[44] Since then, SLIPS surfaces have been fabricated using UV lithography,[45,51,58] electrodeposition,[53] hydrothermal treatment,[75,76] non-solvent-induced phase separation,[49] solution blow spinning,[77] acid-etching[78] and deposition of hydrophobized nanoparticles[79]. These fabrication methods involve either harsh chemical conditions, or complicated multi-step processes that are limited to specific materials and substrates. In comparison, layer-by-layer (LbL) assembly has the advantage of having an extremely simple fabrication process and being applicable to any solvent-accessible surface. Zacharia and coworkers first recognized the potential of
using LbL assembly of polyelectrolytes and acid treatment to fabricate the porous surface for making SLIPS.\textsuperscript{[46]} Aizenberg \textit{et al} came up with a fabrication method utilizing LbL assembly of polyelectrolyte and silica nanoparticles followed by high temperature calcination to obtain the porous structure for infiltrating lubricant.\textsuperscript{[47]} Shiritori and coworkers developed a method of fabricating porous surface by using the LbL assembly of biocompatible polymers followed by porogen removal\textsuperscript{[56]}. Lynn \textit{et al} utilized the reactive LbL assembly by taking advantage of azlactone chemistry to obtain the porous structure to serve as the solid matrix for SLIPS.\textsuperscript{[80]} However, all of the aforementioned methods involve post-fabrication hydrophobicization using perfluorinated species and special post-fabrication modification is needed to achieve porous structure (acid treatment, high temperature calcination, porogen removal, etc.). These additional steps complicate the fabrication process, and limit the type of substrates that can be used to make SLIPS. The post-fabrication modification also brings extra difficulties and increase cost when translating to industrial scale manufacture. Here we report a novel fabrication method of SLIPS involving only the LbL assembly and lubrication step. Neither nanoparticles nor perfluorooctanoic acid are used, both of which have consumer and safety concerns associated with them.\textsuperscript{[81–83]} A superhydrophobic surface with hierarchically rough structure and low surface tension was obtained by LbL assembly of Nafion and branched polyethylenimine (BPEI) in methanol solutions. The porous structure is then infiltrated with krytox\textsuperscript{®}100 to form a SLIPS surface. The entire fabrication process is time saving (less than 10 minutes) and simple, and has great potential to be scaled up for manufacturing an industrial scaled product.
3.2 Experimental Section

3.2.1 Materials

Nafion (20% dispersion) was purchased from DuPont. Branched polyethylenimine (BPEI, MW=25,000), decane, acetone, toluene, silicon dioxide nanopowder, and phosphate buffered solution packs (pH = 7.4) were purchased from Sigma Aldrich. Methanol, sulfuric acid, and hydrogen peroxide (35% w/w in H2O, Cat No. BDH7814-3) were purchased from VWR International. The perfluoropolyether lubricant (Dupont Krytox® PFPE GPL 100) was obtained from Miller-Stephenson. Bovine whole blood (Na-heparin) was purchased from Lampire Biological Laboratories. Deionized (DI) water used in all experiments was produced from a Milli-Q DQ-3 system (Millipore, Bedford, MA, U.S.A.) with resistivity of 18.2MΩ. Naked® juice smoothie, Hidden Valley® Ranch, Sriracha hot chilli sauce, and Welch’s Grape jelly were purchased from a local convenience store. All materials were used as received without further purification.

3.2.2 Hydrophobic PEMs fabrication

For dip coated layer-by-layer (LbL) film, glass slides and silicon wafers were first treated with freshly prepared acid piranha solutions (mixtures of 98% sulfuric acid and 35% hydrogen peroxide at v/v=7/3) for 4 hours at room temperature. The substrates were then rinsed with excess DI water to remove any residual piranha solution on the surface. The substrates were then treated with air plasma for 5 min to activate the surface right before the LbL assembly. For LbL film fabricated on polyethylene terephthalate (PET) film, the substrate was cleaned with DI-water and ethanol followed by air plasma treatment for 5 min right before the LbL assembly. The cleaned substrates were immersed in a BPEI
solution (2.5mg/ml in methanol) for desired time followed by a methanol wash with desired
time, and then immersed in Nafion solution (2.5mg/ml in methanol), followed by another
methanol wash. This process was repeated to create hydrophobic PEMs with desired
number of layers. Spray-coated LbL film was fabricated using travel size spray bottles
(purchased from Target). Three sprays of BPEI solution (5mg/ml in methanol), methanol,
Nafion solution (5mg/ml in methanol), and methanol, were sequentially applied onto a
circular stainless-steel pin to create a bilayer. The cycle was repeated for 10 times and the
substrate was rotate 90° in between each cycle to construct a hydrophobic PEMs.

3.2.3 Impregnating lubricant

A micropipette was used to deliver 8µl/ cm² Krytox®100 onto each of hydrophobic
PEMs and uniform coverage was achieved by tilting the substrate. All lubricated substrates
were placed vertically on Kimwipes for 10 min to remove excess lubricant before testing.

3.2.4 Contact angle (CA) and sliding angle (SA) measurement

Static CA and SA were measured using a ramé-hart CA goniometer. The equipped
auto-dispenser was used to place 5µl droplets for all static CA measurements and 10µl
droplets for sliding angle measurements, and all measurements were repeated for at least
three times. Sliding angle was taken as the smallest tilting angle at which the liquid droplets
started to slide.

3.2.5 Characterization of hydrophobic PEMs morphology

Scanning electron microscopy (SEM) images were obtained using a JEOL-7401
field emission scanning electron microscope.
3.2.6 Self-cleaning experiment

Silicon dioxide nanopowder was sprinkled onto the SLIPS fabricated on PET film. A continuous stream of water from a squeeze bottle was used to completely remove the nanopowder.

3.2.7 Antifouling properties test

Qualitative antifouling property tests were carried out with SLIPS fabricated on PET film with 3 bilayers of BPEI/Nafion PEMs. Both SLIPS and bare PET (negative control) were dipped into bovine whole blood, ketchup, ranch, Sriracha, fruit smoothie, and grape jelly, and then withdrawn from the respective fluids. The processes were video recorded and the appearances of the surfaces after the dipping were extracted from the videos. For the test with bovine blood, the dipping was repeated for 100 times, and the appearances of the surfaces after each 10 dips were extracted from the video.

3.2.8 Flexibility test

The flexibility of the SLIPS (on PET film) surface was tested by first bending the surface either convexly or concavely, and then pipetting water droplets onto the curved surface to see if the surface retains its wetting behavior.

3.2.9 Transmittance properties

The transmittance of bare substrates (glass, PET film, & polyvinyl sticker), PEMs, and SLIPS were measured using UV-VIS spectrometer.
3.3 Result and Discussion

3.3.1 In-situ proton transfer enabled layer-by-layer assembly

The hydrophobic matrix of the SLIPS is fabricated by LbL assembly of BPEI and Nafion in methanol solutions. The schematic illustration of the assembly process is depicted in Scheme 7. The ζ-potential measurements of BPEI and Nafion in methanol solution suggest both polyelectrolytes are neutral, or nearly so, in methanol (Figure 12). It is expected to see a suppression of measured ζ-potential values in organic solvent compared to aqueous solution due to dielectric constant. Additionally, the pKa of protonated amines is much larger than that of the alcohol groups, and the pKa of protonated alcohol groups is much larger than that of the sulfonic acid groups, making the protonation of amine groups on BPEI and deprotonation of sulfonic acid groups on Nafion unfavorable with methanol.

Scheme 7. a) Schematic illustration of LbL assembly of BPEI and Nafion. b) Proposed mechanism of proton transfer from sulfonic acid to amine group resulting in electrostatic attraction.
The protonation and the deprotonation of these functional groups are the reason that BPEI and Nafion carry charges in aqueous solutions. Therefore, the basis for this assembly are somewhat different than that of the conventional aqueous-based electrostatic LbL assembly, where electrostatic attraction between the oppositely charged polyelectrolytes directs the buildup of polyelectrolyte multilayers (PEMs) and the release of counterions and waters of hydration provide an entropic gain. Here, an acid-base reaction mechanism, where protons transfer from the sulfonic acid groups on Nafion to the amine groups on BPEI, is proposed (Scheme 7b). The proton transfer causes the originally neutral BPEI and Nafion to carry charges and then become electrostatically attracted to each other.

The PEMs fabricated with this method showed superhydropobicity. In a previous study, Schlenoff et al carried out LbL assembly of Nafion and a perfluorinated poly(vinylpyridine) in methanol. Even with the use of two perfluorinated polyelectrolytes, the PEMs obtained only show modest hydrophobicity with contact angle (CA) around 110°. In comparison, the PEMs developed in this study possess hierarchical
morphology with microscale fibrous structure and nanoscale particulate structure as revealed by scanning electron microscopy (SEM), leading to the large CA and low drop adhesion. It is not completely understood why such a rough structure can be achieved with this system. Typical LbL assembly does not achieve this, and in fact surface roughness is known to be very dependent on substrate roughness,[85] but that does not seem to be the case here. The neutrality of the polymers in solution is likely not the reason, as adding salt in aqueous polyelectrolyte solutions does not achieve this either. It seems likely that solvent quality and evaporation rate plays a role in creating this rough structure. Methanol is a less good solvent for BPEI compared to water, and Nafion exists as a dispersion. Therefore, upon initiation of the strong acid-based interaction, the polymer complex precipitates more quickly, forming the rough structure. This characteristic is not present in Schlenoff et al’s system,[84] where the perfluorinated poly(vinylpyridine) contains quaternary ammonium groups which are permanently charged. The same assembly of BPEI and Nafion was

Figure 13. Photograph of (BPEI/Nafion)$_{10}$ fabricated by LbL in aqueous solutions.
performed in aqueous solutions, where polyelectrolytes are partially charged. The obtained LBL film surface is smooth (with small rough patches on the edge due to drying) and has contact angle (CA) close to 110° (Figure 13). Therefore, the use of organic solvent is the key to the surface morphology and the surface superhydrophobicity, possibility due to charge suppression and changes in solvent quality.

3.3.2 Fabrication method and optimization

The use of organic solvent for the LbL process enables the buildup of superhydrophobic surfaces. In this study, a superhydrophobic surface with CA of 161.7 ± 4.5° and low adhesion (Figure 14a) is obtained through LbL assembly without any post-assembly modification. However, the surface properties can be affected by several operational parameters during the LbL fabrication. Number of deposition cycles, washing

Figure 14. a) Water contact angle (CA) versus number of bilayers on as prepared LbL film and corresponding SLIPS, (**p<0.01). b) Sliding angle (SA) versus number of bilayers on lubricated LbL films. c) Photographs of water droplets placed on LbL films with 1 to 5 bilayers.
time, dipping time, and drying time between baths can all affect the properties of the resulting PEMs surface. Improper combination of the operational parameters fails to produce PEMs with desired properties. It has long been established that for surface to show superhydrophobicity, the surface needs to have micro/nano rough structure in addition to being chemically hydrophobic. \[^{[34]}\] For modestly rough surfaces that are made with either hydrophilic or hydrophobic material, the Wenzel wetting state is expected to exist. Namely, the rough solid is completely wetted by the liquid, and its apparent CA can be predicted by Equation 2. For hydrophobic and rough solids, the flat surface CA $\theta$ is greater than $90^\circ$ and $r$ is greater 1, and therefore the apparent CA $\theta^*$ is greater than $\theta$. If the roughness $r$ continues to increase, the wetting scheme is called Cassie-Baxter wetting state, where water droplets rest partially on the solid and partially on the air pockets that are trapped within the rough structure. The apparent CA of this wetting model is characterized by Equation 3. Natural surfaces, such as lotus leaf, with hierarchically rough structure can reach the Cassie-Baxter wetting state and show superhydrophobic and self-cleaning properties.

The number of deposition cycles dictates the surface coverage and the amount of material deposited onto the substrates. A certain number of deposition cycles is required to deposit enough material onto the substrate to result in superhydrophobic, self-cleaning surface. Once the minimum deposition cycles are reached, a jump in surface CA is expected, marking a transition from a water pinning Wenzel wetting state to Cassie-Baxter state. With 1-minute dipping and 30-second washing steps between deposition steps, a minimum of 3 bilayers of BPEI/Nafion is required for the PEMs to achieve superhydrophobicity and be used as porous matrix for SLIPS. As shown in Figure 14, PEMs made with one and two bilayers show CA around $105^\circ$, and are water pinning after infused with lubricant. In
contrast, PEMs with 3 bilayers or more exhibit CA over 160° and sliding angle (SA) smaller than 2° after lubrication. This sudden jump in surface CA indicates the switch from

Figure 15. SEM images of PEMs with 1 bilayer (a & f), 2 bilayers (b & g), 3 bilayers (c & h), 4 bilayers (d & i), and 5 bilayers (e & j). Scale bars represent 50µm (a – e) and 1µm (f – j).
The surface morphology of PEMs with different number of bilayers is investigate with SEM imaging (Figure 15). It can be seen that more

Figure 16. Surface SEM images of PEMs with 15 (a), 20 (b), 30 (c), 40 (d), and 50 (e) bilayers, and cross-sectional SEM images of 15 (f), 20 (g), 30 (h), 40 (i), and 50 (j) bilayers. Scale bars represent 100µm (a – d) and 10µm (e – h).
material is deposited on the surface and more rough feature emerges with increasing deposition cycle. Although a number of previous studies show that superhydrophobic surface is not necessary for making SLIPS,\textsuperscript{[47,51]} in this system superhydrophobicity is a strong predictor for the qualification of the surface to become SLIPS after being lubricated.

It is expected that the surface wettability of the PEMs will stay constant beyond minimum deposition cycles. The PEMs with 4 and 5 bilayers have identical surface wettability as the PEMs with 3 bilayers (Figure 14). However, for much thicker PEMs, such as those with 20 and more bilayers, the surface morphology become noticeably different (Figure 16). When the deposition cycles increase to 15, a sheet-like structure starts to form and cover the rough fibrous structure. As more material builds up onto the surface,

Figure 17. Contact angle measure on PEMs with 15, 20, 30, 40, and 50 bilayers.
the sheet-like structure continues to grow and eventually forms a continuum that fully covers the rough structure. This loss in surface roughness is reflected by the decrease in surface CA (Figure 17). From the cross-sectional SEM images (Figure 16), the underlying rough structure resulted from the few initial deposition cycles is still visible. Compared to the rough and porous underlying structure, the top capping sheet is a dense and smooth film. The formation of the sheet-like structure is likely caused by the diffusion limitation within the nanoscale structure. As a result, polyelectrolytes complex over the rough structure and form the sheet-like structure on top. The data suggest that the number of deposition cycle must be large enough to obtain hierarchically rough structure, but small enough to prevent the sheet-like structure from forming.

The surface properties are also susceptible to change of the washing time between BPEI and Nafion solutions during the LbL assembly. The washing or rinsing step during

![Figure 18. SEM images of (BPEI/Nafion)$_3$ PEMs fabricated by LbL assembly with 30 s (a), 1 min (c), and 0 s (e) wash time, the scale bars representing 100 µm. Photographs of water droplets placed on (BPEI/Nafion)$_3$ PEMs fabricated by LbL assembly with 30 s (b), 1 min (d), and 0 s (f) washing time.](image-url)
LBL assembly between polymer adsorption steps is used to remove excess polymer chains that are loosely bound to the surface, making the assembly more reproducible. Without the rinse step, the amount of material remaining on the surface after each polymer bath will be dependent on factors such as withdrawing speed and withdrawing angle of the substrate. Additionally, loosely bound polymer might become desorbed in a latter adsorption step. Although in a previous study, Sun and coworkers utilized the liquid adhered to the substrate right after it is withdrawn from a solution to fabricate a highly transparent and healable antifogging film,[87] for this system removing excess material between polymer baths is critical to obtaining the hierarchical surface structure. The effect of washing time on surface micro/nano structure is summarized in Figure 18. Fibrous structures with different sizes are obtained with 30-second and 1-minute washing time (Figure 18a&c). Longer fibers are obtained with 1-minute wash (48.65 ± 13.94 µm) as compared to 30-second wash (26.55 ± 7.34 µm), but the wetting properties of the film obtained with 30-second and 1-minute wash are indistinguishable (Figure 18b&d). For time efficiency, 30-second wash is taken as the optimal fabrication condition. In contrast, if the wash step is eliminated (0-second wash), no rough structure can be observed with SEM and the surface exhibit a CA close to 110° (Figure 18e&f). The obtained film is also much thicker than those with wash steps. The result shows the wash steps can greatly influence the surface structure of PEMs and surface wettability.

Dipping time is another important operational parameter in LbL fabrication. The length of the dipping time determines the amount of the polymer deposited onto the substrate during each deposition cycle. When the substrate enters a polymer solution initially, a net deposition event takes place, driven by the acid-base reaction between amine
groups and sulfonic acid groups. As the reaction proceeds, the adsorption and dissociation of polymer. If the dipping time is relatively short, only a limited amount of material can be deposited onto the surface. Shorter dipping would require more deposition cycles to reach the same surface coverage and film thickness with longer dipping time. In this study, we focus on developing a fast and facile fabrication process. Therefore, an adequately long dipping time coupled with fewer number of deposition cycles is favored. Dipping time is varied from 10 s to 2 minutes, while the number of deposition cycles and washing time are held constant at 3 cycles and 30 s, respectively. The surface CA of the resulting films are measured (Figure 19a). With 10 s and 30 s dipping, the resulting films exhibit surface CA around 140°, and water droplets pin on the surface after lubrication. As the dipping time further increases to 1 minute and 2 minutes, superhydrophobic surfaces with CA close to 160° are obtained. The differences in surface morphology are shown in Figure 20. While nanoscale structures of the surface fabricated with various dipping time are similar, the microscale fibrous structure is much thicker and longer for films with longer dipping time.
It can be concluded that the dipping time has to be long enough to allow adsorption of adequate material. Although dipping time can affect the surface properties of PEMs, it is a less prominent factor than deposition cycles and washing time in affecting surface morphology.
The surface wettability is found to be most sensitive to change of drying time between baths. Drying can have multiple effects on the LbL films. It locks the polymer chains in certain conformation, which ultimately affects the film morphology. Drying between baths also forces excess amount of material onto the surface. Considering the high volatility of methanol, the drying will take place extremely fast, thus having strong impact on surface properties. To test the influence of drying on surface properties, the surface is

Figure 21. SEM images of PEMs with 0 s (a & e), 30 s (b & f), 60 s (c & g), and 120 s (d & h) drying time. Scale bars represent 50 µm (a – d) and 1 µm (e – h).
allowed to stand in air for various time periods between each bath. The surface wettability of PEMs fabricated with various drying time is characterized with CA measurements (Figure 19b). If the surface is held for only 30 s in air between baths, the surface CA decrease from 162° to 127° and longer drying times cause further losses of hydrophobicity. The PEM films obtained with drying are inhomogeneous as well. The surface morphology was characterized by SEM images (Figure 21). Although the nanoscale structures of PEMs with drying are similar to that of films without drying, the microscale structure is very different. The surfaces still possess some fiber-like structures, but the fibers are much longer and chaotically tangled together. Sheet-like structures and chunks of aggregates are also observed. The dramatic change in surface morphology caused by drying is the origin of the decrease in surface CA. Perhaps drying between steps allows for rearrangement of the polymer chains at the surface in air, influencing subsequent deposition steps.

The final optimized fabrication process has 1-minute dipping time, 30-second washing time, and 3 deposition cycles. This results in a total fabrication time close to 9 minutes. Our method is compared to some other fabrication methods of superhydrophobic surfaces summarized in a previous study,\textsuperscript{[88]} and this information is also summarized in Table 1. Our strategy is considerably faster than most of the methods listed and results in much smaller SA than does the rest of the methods.

Table 1. Comparison of our method and some other facile methods reported in previous studies for fabricating superhydrophobic surfaces.\textsuperscript{[88]}

<table>
<thead>
<tr>
<th>Surface</th>
<th>Process time</th>
<th>Static contact angle (°)</th>
<th>Sliding angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our method</td>
<td>9 min</td>
<td>161.7 ± 4.5</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Rough Polystyrene</td>
<td>5 s</td>
<td>152.1 ± 1.8</td>
<td>13.9 ± 3.8</td>
</tr>
<tr>
<td>Nanoporous PDVB chalk</td>
<td>28 hr</td>
<td>151.3 ± 1.4</td>
<td>7.4 ± 1.5</td>
</tr>
</tbody>
</table>
Spray-deposited silica nanoparticles  4 hr  151.7 ± 1.1  5.8 ± 2.4
Dip-coating and SAM  9 hr  137.7 ± 14.5  55.5 ± 5.2
Porous BMA-EDMA  1 hr 15 min  160.2 ± 0.6  5.7 ± 1.1
Modified HEMA-EDMA  4 hr 15 min  152.0 ± 3.6  6.3 ± 1.6
Candle soot  unknown  151.6 ± 1.7  11.3 ± 2.1
Commercial coating (Ultra-Ever Dry)  unknown  154.7 ± 1.4  14.8 ± 3.4

3.3.3 SLIPS criteria

SLIPS criteria are previously discussed in Chapter I. From Equation 5 and 6, it can be concluded that larger $r$ and $\phi$ result in smaller value of the left-hand side of the equations, and therefore more likely to yield the emerged regime. Given the fact that the surface consists of irregularly rough structure and nanoscale particulate structure, it is difficult to evaluate exactly the $r$ and $\phi$. However, qualitative analysis of the change in surface morphology can still provide valuable insight about why the SLIPS criterion is met with certain surface morphologies.

Increasing dipping time and number of deposition cycles have similar effects on the surface morphology. With longer dipping or more deposition cycles, the obtained fibrous structures are thicker and have surface density (Figure 15 & 21). These result in both larger $r$ and $\phi$. Once $r$ and $\phi$ are large enough to satisfy Equation 5, the wetting regime switches from impaled to emerged, and the lubricant-infused surface transforms from water-pinning to water-sliding. Similar analysis can be made with surface fabricated with different washing time. When washing steps are eliminated, the obtained surface is very flat (Figure 18e). With both $r$ and $\phi$ approach to 1 from opposite directions, the left-hand side of Equation 6 goes to 0 and the equation is satisfied. This results in the impaled wetting
mode and a water-pinning surface. In the case of surfaces made with various drying time, the situation is different. With longer drying time, the surfaces show more rough structures, or larger $r$ and $\phi$, but are water-pinning after infusing with lubricant. This can be explained by the Varanasi and coworkers’ previous study, where they find that decreasing spacing between rough features decreases droplet mobility under emerged regime.[51] When $\phi$ becomes extremely large, even though the emerged regime is satisfied, the bottom of the droplet is mostly making contact with the solid texture and only a small fraction of it is sitting on lubricant. The water-lubricant interface is the key for the SLIPS to be slippery.[48] This explains why longer drying time yields rougher but water-pinning surfaces.

3.3.4 Omniphobicity and antifouling properties of SLIPS surface

The SLIPS possess the omniphobicity against aqueous solutions as well as a variety of organic solvents with a wide range of polarity (Figure 22a). Droplets of water, toluene, ethanol, decane, and acetone can easily slide down the SLIPS. In addition, the SLIPS can also repel methanol, from which the surface is fabricated. The SAs for most of the tested fluids on SLIPS are well below 5°, except for acetone and methanol, which have SAs slightly higher than those for the rest of the probing fluids, but are still reasonable low (close to 10°). Due to the simplicity and versatility of LbL assembly, we are able to fabricate the BPEI/Nafion PEMs on surfaces made from a wide spectrum of materials. Stiff inorganic substrates, including glass slides, silicon wafers, and stainless-steel pins, and flexible polymer substrates, including polyethylene terephthalate (PET) films and commercially available polyvinyl stickers, are all used to fabricate SLIPS. The water CA and SA of SLIPS fabricated on glass slide, stainless-steel pin (spray coated), and PET film are summarized in Figure 22b and corresponding CA of various probing liquids are shown.
in Figure 22c. The results indicate that the wetting properties of the SLIPS is not substrate-specific, since no statistically significant differences are observed in water CA and SA of SLIPS fabricated on glass slides, metal pin, and PET films.

![Figure 22.](image)

Figure 22. a) Contact angles (CA) and sliding angles (SA) of various solvents on SLIPS. b) Water contact angles (CA) and sliding angles (SA) on SLIPS fabricated on glass slide, stainless steel, and PET film. c) Photographs of droplets of various solvents placed on SLIPS. d) SLIPS-coated and bare PET films are dipped into bovine whole blood for 100 times to assess the antifouling property of SLIPS against blood. e) SLIPS-coated and bare PET films are dipped into ketchup, ranch, sriracha sauce, juice smoothie, and grape jelly to evaluate the antifouling property of SLIPS against complex fluids.
SLIPS have been shown to possess outstanding antifouling properties against biological fluids and biofilm formation.\cite{56,69} To demonstrate the potential application of our LbL-fabricated SLIPS on medical devices, its ability to resist blood stain is evaluated qualitatively. As shown in Figure 6d, both the bare and SLIPS-covered PET films were dipped into bovine whole blood for 100 times. The bare PET film was completely covered with blood after only one dip, while the SLIPS surface remained mostly unfouled with only a few spots being stained by blood after 100 dips in bovine whole blood. These surface defects are likely caused by the loss of lubricant due to shear force.\cite{72} We emphasize here that during this experiment, the lubricant layer was experiencing maximum shear stress with the surface entering and exiting at the direction perpendicular to the air-blood interface. If the surface were positioned parallel to the interface during dipping, less shear force should be experienced. In addition to biological fluid, the SLIPS surface can also prevent the stain of some common complex and viscous fluids, including ketchup, ranch, sriracha, juice smoothie, and grape syrup (Figure 22e). The antifouling properties against these fluids shows the potential of SLIPS to be used in food packaging applications.

3.3.5 Optical properties, flexibility, and self-cleaning

Other than being omniphobic and antifouling, the LbL-fabricated SLIPS developed in this study possess some additional properties that make them easy to be incorporated into practical applications. The SLIPS also demonstrate self-cleaning property as shown in Figure 23a. Silicon dioxide nanopowder is spread onto SLIPS coated PET film and the powder stick to the surface immediately. The stuck dust can be easily washed off by a water stream, leaving no traits of either the powder or water left on the surface. The SLIPS can be very flexible if they are fabricated on polymer substrates. This allows the SLIPS to be
applied to surfaces with various curvatures. However, for this to happen, the SLIPS need to keep the omniphobicity under mechanical stresses. The surface wettability of SLIPS coated PET film with bending is therefore assessed (Figure 23b). As demonstrated, water droplets can easily slide down on both concavely and convexly bent SLIPS. It shows that the SLIPS developed in this study is able to retain the surface properties under reasonable bending and can thus be applied to curved surface. As shown in Figure 23c, the BPEI/Nafion PEMs is opaque, but becomes highly transparent after infused with lubricant. The optical transmittance of bare substrates (glass slide, PET film, and polyvinyl sticker),
PEMs coated surfaces, and SLIPS coated surfaces are summarized in Figure 23d. The transmittance of SLIPS coated surfaces is very close to that of the bare substrates. In case of glass slide, the transmittance of SLIPS is even higher than that of the bare glass slides, due to reduction in reflectance. The superior optical property of the SLIPS allows the application of our film as surface protectors in highly specialized fields such as medical devices, and photo sensing devices.

3.3.6. Easy incorporation in practical applications

Due to the excellent optical property, self-cleaning and flexibility, the SLIPS can be easily incorporated in practical applications. To demonstrate the easy incorporation of LbL SLIPS to practical applications, the SLIPS is fabricated on commercially available polyvinyl stickers. The SLIPS coated sticker was also applied to a glass slide as shown in Figure 23e. Half of a 25mm×25mm glass slide is covered with the polyvinyl sticker. The appearance of the bare glass area and the area covered with polyvinyl sticker can hardly be distinguished from each other due to the superb optical properties of the SLIPS. However, the surface wettability of the two areas differs greatly. Water and blood droplets pin on the bare glass (inclined at 30°), but easily slide down the SLIPS coated area. The SLIPS can endow the surface with hydrophobicity and self-cleaning property, which would simplify the maintenance and cleaning procedures. By fabricating the SLIPS onto commercially available membranes/stickers, they can be easily applied to various surfaces due to their exceptional flexibility. Moreover, the stick-on membranes can be easily replaced once the SLIPS lose their properties due to drainage of lubricant or surface mechanical damage. We envision that this SLIPS membrane/sticker will be widely utilized in many applications, because it can be easily installed and replaced. In addition, the SLIPS have been proved to
have a long shelf-life, a requirement for industrial use. The CA and SA of multiple SLIPS samples are monitored over 60 days (Figure 24), and the result indicates that the SLIPS can remain slippery for at least 60 days.

Feasibility of mass production is crucial to potential commercialization of SLIPS type surfaces. The facile and fast fabrication method developed in this study provides the possibility of scaled-up fabrication of SLIPS. The fabrication process demonstrated here involves sequential dipping, and PEMs can be deposited onto flexible polymer substrates, it is expected that industrial fabrication methods, such as roll-to-roll, might be suitable for mass production of SLIPS onto polymer membranes. In addition to using dip-coating, spray coating can also be used to make SLIPS onto stainless steel pins. As shown in Figure 25, the superhydrophobic surface can be achieved with 10 bilayers using spray coating technique. Although spray coating has higher number of bilayers requirement than does

Figure 24. Contact angle and sliding angle evolution over 60 days.
A novel fabrication method, involving only LbL assembly and lubrication step, is developed for making SLIPS. The LbL assembly is driven by an in situ proton transfer between BPEI and Nafion in methanol. The reported fabrication method achieves both direct buildup of hydrophobic materials and formation of hierarchical structure with the LbL assembly, and thus requires no post-fabrication modification to realize superhydrophobicity. By using the LbL assembly of BPEI and Nafion in methanol, SLIPS are fabricated on a variety of substrates, including both stiff and flexible surfaces. The SLIPS exhibit outstanding omniphobic, antifouling, and self-cleaning properties, and they
can be highly transparent and flexible if the substrates possess these properties. The facile and fast fabrication process offers the possibility for large scale fabrication of SLIPS.
CHAPTER IV

FUTURE WORK

4.1 Multifunctional SLIPS

Chapter II describes the fabrication of thermally-responsive smart SLIPS, which exhibit distinctive wetting behavior under various temperatures, was demonstrated. The fabrication was accomplished by infusing the LbL assembled hydrophobic nanoparticulate porous matrix with a thermally reversible gel. Future work should explore the possibility of introducing other useful functionalities to the SLIPS.

Dual functional surfaces with both anti-biofouling property and selective binding ability to biomolecules can serve as test platforms for diagnostics of various diseases by detecting biomarkers in the biological systems. Fabricating bioactive SLIPS was previously investigated at Harvard Medical School in corporative project. The design of the dual functional surface involves chemically immobilizing antibodies onto the solid matrix. As the some of the top feature of the porous solid matrix protrudes out of the lubricant layer, the antibodies which are attached to those areas can make direct contact with the test fluid (Figure 26a). Because overall the solid matrix remains hydrophobic, the porous structure can still hold the lubricant in place and the surface is overall antifouling.
Previous work has focused on optimizing the ratio between hydrophobic groups and bioactive moieties. However, with the silica nanofilament used in previous study (Figure 26b) can only provide irregular porous structures that can differ largely from sample to sample. The amount of solid feature that protrudes out of the lubricant is uncontrollable and is likely to be less than potent for the testing purpose. In addition, with the current strategy, in which the infusing of lubricant is the last step, the majority of the immobilized antibodies are submerged under the lubricant and cannot make direct contact with test fluid and are therefore wasted.

Future study on this topic should focus on developing new design based on well-defined surface structures, such as lithographically patterned micropost array.\cite{51} These surfaces have microscale features of the same height throughout the entire surface. The top facets of the microposts are expected to be directly exposed to test fluid under impregnated regime as discussed in Chapter I. Therefore, the availability of bioactive moieties can be controlled. A further challenge would be to selectively modify the top facets with bioactive agents and the side facets with hydrophobic groups. The hydrophobic grooves can hold the lubricant in place and the top facets can provide specific binding sites for biomarker detection.
4.2 LbL in organic solvents for fabrication of hydrophobic matrix for SLIPS

Chapter III demonstrated the use of methanol as solvents in LbL assembly of BPEI and Nafion resulted in direct fabrication of superhydrophobic surfaces, which are served as the porous matrices for SLIPS. It is believed that the poor solvent quality enables the formation of hierarchically rough structure, and the unique acid-base reaction drives the buildup of the polyelectrolytes. Due to the simplicity and the time saving nature of the method, it has great potential for large scale fabrication of SLIPS. Pilot trial was carried out on the roll-to-roll line in the National Polymer Innovation Center on PET films. So far, the resulting surfaces failed to recapitulate the properties of lab-scaled products. The main problem with the current apparatus is that the drying time between baths are too long. Films are completely dried when entering to the next bath. As shown in Figure 21, extended drying time can greatly affect the surface wettability. Therefore, further investigation on large-scale fabrication of SLIPS using this system should focus on developing a new roll-to-roll apparatus which has a short belt travel time between baths.

The previous study shows that both the hydrophobicity and rough structure can be obtained at the same time with the use of methanol in LbL assembly. A survey study of organic solvents other than methanol should be conducted to investigate the possibility of using other solvents to make this surface. Insights on how the solvent properties, such as polarity, proticity, and dielectric constants, affect the surface structure and surface properties of the LbL film can be obtained. It was shown previously that the use of acetone and ethanol can produce similar surface with BPEI and Nafion as compared to methanol. However, acetone caused the degradation of BPEI as evidenced by the color change of both the BPEI solution and PEM to yellow. Therefore, the PEMs fabricated with LbL
assembly in acetone was not further studied. A wider range of solvents should be carefully selected to carry out this LbL assembly and the surface structure, morphology, and wettability of the resulting PEMs should be investigated.
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