

Functional polyelectrolyte multilayer assemblies for surfaces with controlled wetting behavior

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ABSTRACT: Controlled wetting at surfaces and interfaces is an important area of research with numerous potential commercial applications. Both superhydrophobicity and superhydrophilicity can be used to enable applications such as self-cleaning, dropwise condensation, or antifogging. Many strategies for creating such surfaces center around biomimicry, replicating the structure of the lotus leaf, for example. Given the potential impact, creating surfaces with these properties using any number of fabrication is of great interest. One very promising fabrication technique, however, for creating these surfaces is the layer-by-layer (LbL)-directed self-assembly of polyelectrolytes and other charged materials. LbL is a sequential adsorption technique wherein a surface is exposed to first a solution of one charge and then a solution of the opposite charge. LbL has many advantages, including the ability to incorporate many different types of materials and therefore functionality, the ability to conformally coat substrates of complex geometry, and environmentally friendly aqueous processing. This review describes recent progress in using LbL to create surfaces with controlled wetting. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42767.

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INTRODUCTION

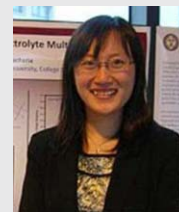
Of many nanofabrication methods, the aqueous-based layer-by-layer (LbL) assembly technique has attracted significant interest owing to its simplicity and versatility, which has been widely used to fabricate nanostructured materials with precisely tailored properties.^{1,2} Typically, the films are made of two oppositely charged polyelectrolytes or colloidal materials bound together through electrostatic interactions,^{2,3} assembled with a sequential dipping or spraying process.^{1,3} Exploring the functionalities of LbL films is a highly active research area, incorporating a broad range of materials^{1–10} (including polymers, nanoparticles, metal ions, lipids, proteins, dye molecules, dendrimers, and quantum dots) using various substrates. These materials are assembled not only with electrostatic interactions^{2,3} but also with hydrogen bonding,^{2,4} hydrophobic interactions,^{5,6} coordination interactions,^{3,7–9} covalent bonding,¹¹ hydrophobic interactions, and complementary based pairing.^{6,12,13} LbL assembly can be applied to a wide range of textured and curved surfaces, and there are many diverse potential applications for LbL materials.^{3,13} Some examples are drug delivery,¹⁴ antimicrobial coatings,¹⁵ self-healing coatings,¹⁶ anti-corrosion coatings,¹⁷ flame-retardant coating,¹³ superhydrophobic coatings,¹⁸ omniphobic slippery surfaces,¹⁹ light-emitting

diodes,² electronically conductive films,² electrochemically reversible capsules,² electrolytes,² proton exchange membranes and direct methanol fuel materials,² lithium-ion batteries,¹³ organic field-effect transistor,¹² electrochemical capacitors,¹³ and photovoltaic and biosensors.²

The ability to control wetting at surfaces and interfaces has the potential to impact many areas, and is the subject of many review papers, especially based on biomimetic strategies.^{20–22} These include using superhydrophobic surfaces for saving energy, for example, reducing frictional energy dissipation at solid-liquid interfaces,^{23,24} and creating dropwise condensation to improve heat transfer rates,²⁵ improve product lifetimes, such as self-cleaning surfaces,²⁶ or to be used in new technologies such as microfluidics. Superhydrophilic surfaces are of interest for applications such as antifogging²⁷ and evaporative cooling.²⁸ Superoleophobic or superoleophilic materials may be of potential use for oil/water separations.²⁹

Superhydrophobic surfaces have most commonly been made by mimicking the lotus structure that has a hierarchical texture. In this case, superhydrophobicity denotes not only a high (>150°) static water contact angle but a very low (<10°) roll off angle, making the surface self-cleaning. Such surfaces have been made using various approaches, such as creating a textured rough

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surface covered with low surface energy molecules, roughening the surface of hydrophobic material, and generating well-ordered microstructure surface with a small ratio of the liquid–solid contact area.^{30–32} However, some of the practical difficulties associated with creating textured rough surfaces via methods such as sol–gel,³³ electrochemical deposition,³⁴ photolithography,³⁵ or colloidal templating³⁶ are that they are hard to apply to curved surfaces. They tend to be poorly adhered to the substrate,³⁷ and they can be difficult to scale. The LbL process may be able to overcome these difficulties.¹⁸ Polyelectrolyte multilayers (PEMs) can be fabricated with controlled thickness at the molecular level and controlled chemistry based on the assembly components and conditions (such as pH, salt, and concentration).⁶ Another advantage of working with PEMs is the ease with which they can coat curved surfaces with no additional adhesion layer required. However, the water-based LbL assembly process is based on the adsorption process in which the layers are constructed one at a time, which is time consuming.³ Recently, spray LbL assembly has been shown to considerably shorten the assembly process.^{1,6,38} As the assembly is typically made from materials that are water soluble, the surface chemistry of LbL coatings is often hydrophilic, including several superhydrophilic examples (i.e., contact angle less than 10°).³⁹ Creating superhydrophobic surfaces and other types of surfaces with controlled wetting from LbL is an active area of research.

This review focuses on the recent progress in controlling surface wettability using PEM thin films based on the LbL technique. This includes self-cleaning liquid repellent surfaces that mimic natural materials such as the lotus leaf,^{19,32–38,40–43} water pinning surfaces that have a very high static contact angle but exhibit strong adhesion to water drops,⁴⁴ and superhydrophilic³⁹ surfaces with extremely low static contact angles. Moreover, progress in this area has extended to develop further functionalities including antibacterial surfaces,^{15,45–47} antifogging surfaces,⁴⁸ anti-icing surfaces,⁴⁹ self-healing,^{10,16,38,50} antireflective surfaces,^{51,52} reversible switchable wetting from superhydrophobicity to superhydrophilicity with both PEMs and polyelectrolyte brush

surfaces,^{31,53–63} liquid flow guiding via patterns,^{30,64} wettability gradients,^{65,66} and superhydrophobic patches in microchannels.⁶⁷

SUPERHYDROPHOBICITY AND SUPEROLEOPHOBICITY: BIO-INSPIRED SURFACES

Early in 1996, Onda *et al.*⁴¹ reported super-water-repellent fractal surfaces created with low surface energy materials on rough surfaces. From that time, methods to fabricate superhydrophobic surfaces have attracted a great deal of focus. Many natural surfaces including plants (i.e., lotus leaf) as well as parts of insects (i.e., legs of the water strider)³⁰ exhibit such properties. Water droplets completely bead up on these surfaces, with static contact angles greater than 150° and are easily shed from these surfaces with low contact angle hysteresis (<10°).^{42,43} The most famous example of superhydrophobicity is the lotus effect, where hierarchical micro/nanostructures maintain air pockets so that form a stable interface between surface and the applied liquid—Cassie state [Figure 1(C)].^{68,69} The wetting on a smooth surfaces depends on the chemical properties on the surface, but roughness will enhance either hydrophobicity or hydrophilicity. To achieve low contact angle hysteresis on a hydrophobic surface, the geometry (hills and valleys) should ensure low contact area between water and the surface (Cassie state instead of Wenzel state). In the context of LbL systems, the addition of a nanoparticle is often required to achieve this texture, although some exceptions to this will be described. Furthermore, a low surface energy molecule with as fluorinated or alkyl silane is also almost always applied to the surface as the last step. In this way, water is interacting with this chemistry and not with the ionic groups of the PEM that have a much higher affinity for water.

Shiratori and coworkers⁷⁰ first reported a superhydrophobic coating created from PEMs using poly(allylamine hydrochloride) (PAH), poly(acrylic acid) (PAA), and silica (SiO₂) nanoparticles. After removing the polymers, the remaining SiO₂-textured structure was coated with a monolayer of a low surface tension fluorinated silane. An alternate approach has been developed by Zhang and coworkers³⁴ with a LbL film coating a

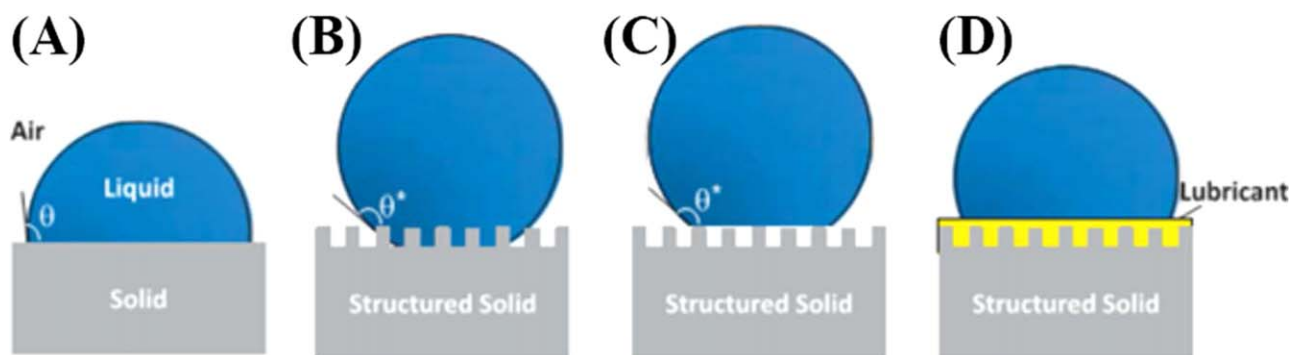


Figure 1. Wetting on smooth and structured surfaces. A liquid droplet sitting on (A) a smooth surface with an intrinsic contact angle, (B) a textured surface that is completely wetted by the liquid, known as a Wenzel state droplet, (C) a textured surface with trapped air pockets, known as a Cassie state droplet, and (D) a textured surface that is infused with an immiscible lubricating fluid (or slippery liquid-infused porous surfaces, SLIPs). (Reproduced from Ref 40, with permission from Materials Research Society). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

textured surface made from dendritic gold clusters on indium tin oxide (ITO). Rubner and coworkers,¹⁸ however, demonstrated that the requisite textured surface for a superhydrophobic coating can be achieved with a honeycomb-like porous PEM with a further SiO₂ nanoparticle coating. This porous multilayer was assembled from PAH and PAA and then treated with acidic solutions. After crosslinking the porous structure and coating with SiO₂ nanoparticles, a fluorinated silane is deposited on the surface to achieve superhydrophobicity. Covalently crosslinking the PEM both preserves the texture and highly reduces swelling when the film is then exposed to water.

A similar honeycomb structure can also be achieved via silicon etching.⁷¹ The geometry of these honeycomb structures is easily tuned to modulate the superhydrophobicity. Instead of a honeycomb-like structure, a hierarchical porous structure can also be fabricated by simple polyelectrolyte/silica nanoparticles assembly, which can create the appropriate roughness for a superhydrophobic surface.^{72,73} Also, polyelectrolyte/silica multilayers have been applied onto cotton fabrics to create superhydrophobic coatings.⁷³ A first bilayer of PAH/PAA enhances adhesion to the cotton fibers, after which a rough silica nanoparticle-containing multilayer of PAH/SiO₂ and finally a fluorinated silane are applied to the cotton to achieve superhydrophobicity. A raspberry-like polystyrene/silica (core/shell) structure can be used during LbL assembly instead of silica nanoparticles. After calcination, the porosity is much higher (~50%) with a hollow core-silica shell structure, which is an ideal hierarchical structure for both superhydrophilic and superhydrophobic surfaces and the superhydrophilic version has excellent antifogging properties.⁷⁴

Although most of the examples given here require the inclusion of some type of inorganic nanoparticle, there are examples of hierarchical structures that can be produced with other types of LbL assembly or postassembly modification.^{75–78} Sun and coworkers^{75,76} reported an all organic superhydrophobic surface made from an LbL film of PAA co-assembled with a positively charged polyelectrolyte complex of positively charged diazoresin (DAR) and negatively charged PAA⁷⁵ and hydrogen-bonded complex of poly(vinylpyrrolidone) and PAA.⁷⁶ The roughness increases with deposition of bilayers during the first few assem-

bly cycles, which therefore results in the correct roughness for a superhydrophobic surface. Lynn and coworkers report a so-called reactive LbL route to creating superhydrophobic surfaces while using neither nanoparticles nor fluorinated molecules. Their surfaces are made by the alternate deposition of poly(2-vinyl-4,4-dimethylazlactone) (PVDMA) and poly(ethylene imine). It was found that if the PVDMA solution also contained PDVA oligomers the resultant surface was extremely rough and superhydrophobic (contact angle > 150°).⁷⁷ However, this superhydrophobicity is not indefinitely stable if the film is submerged under water; the property lasts a matter of days. If the surface is further functionalized with aliphatic amines (or semifluorinated amines), the superhydrophobicity was seen to last for at least 6 weeks. Furthermore, if these polymers are deposited onto surfaces using organic solvents, materials that are water soluble such as sugar cubes or salt crystals can be coated in a superhydrophobic layer and made to be water impermeable.⁷⁸ In another strategy that does not use nanoparticles, although is an organic–inorganic composite structure, hierarchical vertically aligned silver nanoflakes can be created via exploiting lateral compressive stress of surface wrinkles.⁷⁹ Yoo and coworkers⁷⁹ incorporated silver ions in linear poly(ethylene imine) (LPEI)/PAA multilayered coatings, which formed vertically aligned nanoflakes during silver reduction. The ordered nanoflakes enabled the creation of a superhydrophobic surface over a large area when treated with a fluorinated silane (Figure 2).

Instead of the time-consuming dipping LbL assembly followed by fluorinated silane deposition, Sun and coworkers³⁸ have also developed a fast-spraying LbL method to fabricate a mechanically robust, self-healable superhydrophobic coating, based on a highly porous and rough [PAA/PAH-SPEEK LbL film, assembled from PAA and PAH-SPEEK (sulfonated poly(ether ether ketone))] complex, with a low-surface energy healing agent 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS) and perfluorooctanesulfonic acid lithium salt (PFOS) all created simply by spraying. The spraying of the low-surface energy healing agent instead of using vapor deposition enables application of the coating outdoors and on a large scale. Moreover, the low surface energy agent from the porous reservoir can be refilled easily by respraying the agent.

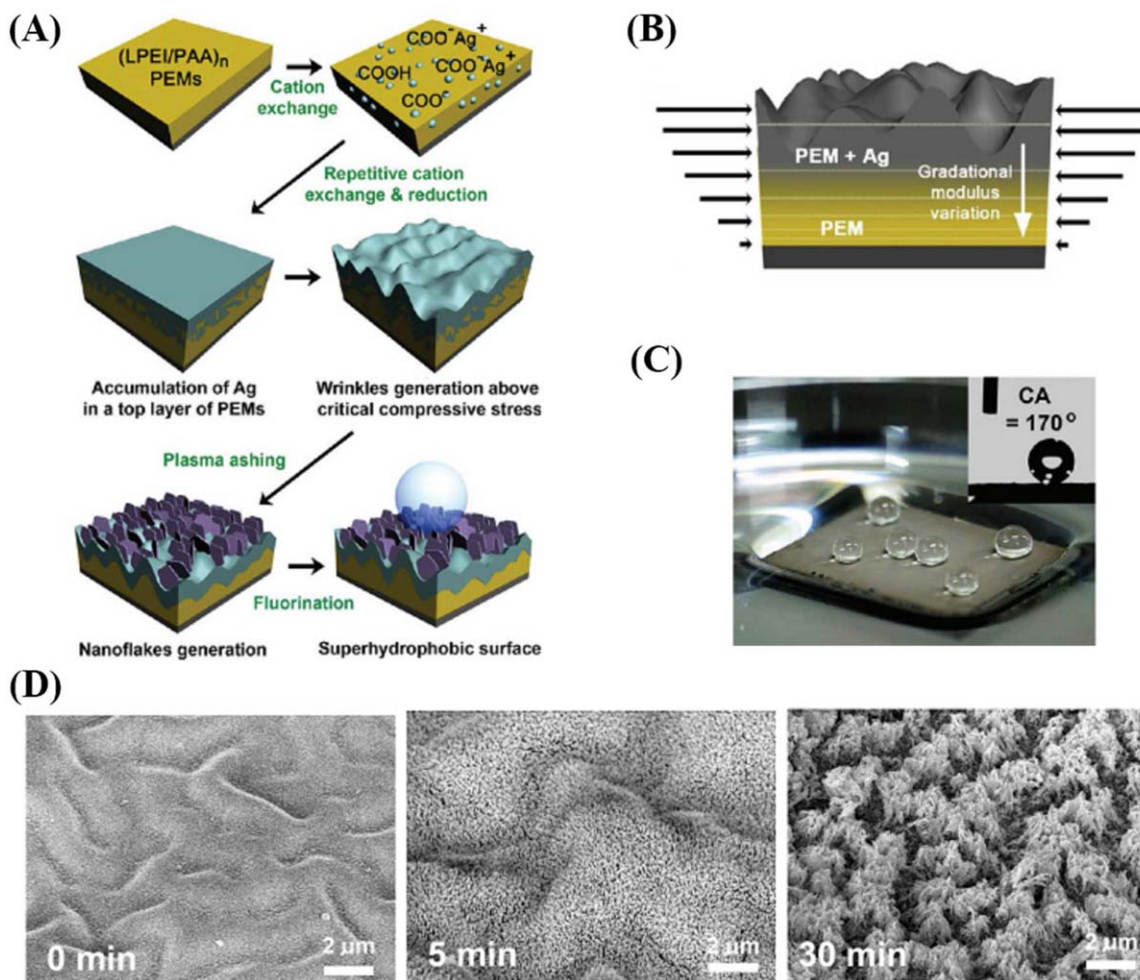


Figure 2. Large-area superhydrophobic surface made from vertically aligned nanoflakes with wrinkling. (A) Schematic illustration of the silver nanoflake structure. The sequential procedures include PEM deposition, counterion exchange and silver reduction, surface wrinkling, and plasma etching for creation of nanostructure and superhydrophobic monolayer modification. (B) Schematic of the gradation in modulus of the polyelectrolyte complex film due to the silver reduction. (C) Superhydrophobic property ($\sim 170^\circ$) of the vertical aligned nanoflake arrays. (D) SEM images of the evolution of surface texture with varying plasma etching time, wrinkled from 0 to 30 min. (Reproduced from Ref 79, with permission from American Chemical Society). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A “sticky” surface, or one that pins water, has high contact angle hysteresis [Wenzel state, Figure 1(B)] as well as a high contact angle, meaning water drops bead up and then adhere to the surface. This adhesive property also has natural examples such as rose or other flower petals or gecko feet.⁴⁴ Two factors contribute to increasing contact angle hysteresis—roughness and chemical defects (heterogeneities).^{80,81} Su and coworkers⁸² used LbL polyelectrolyte assembly to create a surface with quantified surface heterogeneities and studied the relationship between contact angle hysteresis as the area fraction of the defects. Compared with a POTS surface, which is uniform and hydrophobic, a PEM surface hydrophobized with perfluorooctanoate anion (PFO⁻) counterion exhibits similar static and advancing contact angle, but still has numerous hydrophilic defects from the underlying multilayer. This kind of surface, therefore, exhibit much larger contact angle hysteresis ($\sim 97^\circ$) compared with the POTS surface ($\sim 10^\circ$) on the substrates of same roughness. Ji and coworkers⁷¹ reported the fabrication of

larger scale defects. After LbL assembly of PEI/PAA on hexagonally patterned PDMS arrays, sticky superhydrophobicity was observed, which transitioned to a self-cleaning superhydrophobicity as the PDMS surface was fully coated. Zacharia and coworkers⁸³ report a rose-petal-inspired LbL assembly of ionic raspberry-shaped particles to create a water pinning surface capable of pinning water with a force of as much as $\sim 600 \mu\text{N}$, compared to $\sim 75 \mu\text{N}$ for a natural rose petal.⁴⁴ Their surface is also oleophilic in air and oleophobic under water similar to reported nacre-inspired surface.^{83,84}

Surfaces that resist liquids with both high (water) and low (oil) surface tension values are known as omniphobic.^{85,86} Omniphobicity has broad practical applications for self-cleaning, antifouling, stain-free clothing, spill-resistant protective wear, refinery processes, and fuel transportation. It is possible to create an omniphobic surface based on complex re-entrant geometries,^{85,86} wherein droplets are pinned at the edges of the micro/

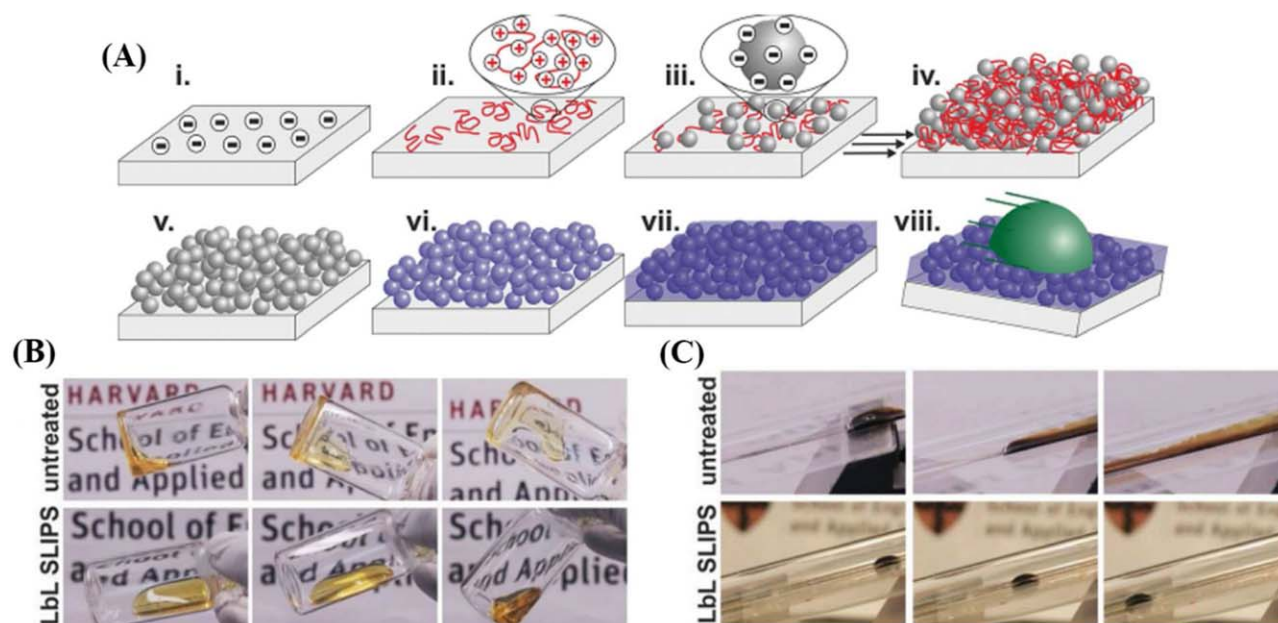


Figure 3. Transparent, omniphobic slippery lubricant-infused porous coatings (SLIPS) using LbL assembly. (A) Schematic illustration of LbL omniphobic slippery lubricant-infused porous coating. Negative charges are introduced to the substrate (i) and subsequent layers of positively charged polyelectrolyte PDDA, (ii) and negative charged silica nanoparticles (iii) are adsorbed to form a hybrid multilayered thin film (iv) that can be calcined to produce a porous silica coating (v). After covalently functionalizing the surface with fluorinated silane (vi), the fluorinated lubricant is infused into the coating (vii), forming an omniphobic, slippery (viii). The coatings repel different complex fluids on curved surface. (B) Time-lapsed images of SLIPS coating repel honey in the inside of a glass vials and (C) crude oil in the inside of the coated glass tube. In comparison, both honey and crude oil stick to the untreated glass vial/tube. (Reproduced from Ref 91, with permission from Wiley). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanostructures thereby preventing their penetration. Using electrospinning⁸⁵ or simple dip-coating processes,⁸⁷ Cohen and coworkers^{85,87} show us the importance of the geometry and the spacing, critical design parameters for this property. Textured silicon coated with cellulose-containing LbL films has been shown to be oleophobic as well.⁸⁸ Oleophobic but hydrophilic⁸³ as well as oleophilic but hydrophobic surfaces have also been created with LbL as well.⁸⁹

Recently, a conceptually different approach was developed to creating omniphobic surfaces inspired by the slippery *Nepenthes* pitcher plant.^{33,90} The surface consists of a continuous thin film of lubricant locked in place by a micro/nanostructured substrate [Figure 1(D)], and these surfaces are called SLIPSs. Unlike lotus-type structures, which rely on a compressible gas layer between the surface and the liquid to be repelled, a SLIPS surface uses an incompressible liquid or lubricant. SLIPS surfaces outperform natural analogs in terms of liquid repellency. These surfaces repel water, organic solvent, oil, blood, and so forth, with low contact angle hysteresis ($<2.5^\circ$).⁹⁰ Zacharia and coworkers¹⁹ first recognized the potential of LbL to create a lubricant-infused omniphobic repellent surface. A microporous reservoir for the lubricant is fabricated by staged acid etching of a branched poly(ethylene imine)/PAA (BPEI/PAA) film. The film performs well but is not transparent due to the scattering of light by the microscaled features. Aizenberg and coworkers⁹¹ overcome the transparency issue by LbL assembly of poly(diallyldimethyl ammonium chloride) (PDDA) and negatively charged silica nanoparticles (20 nm) (Figure 3). This film is cal-

cined to remove the organic component, creating porosity, a fluorosilane is vapor deposited, and the lubricant is infused into the material. Shiratori and coworkers⁹² reported an antireflective LbL SLIPS film made from chitin nanofiber and silica nanoparticle with high transmittance ($\sim 97\%$) and low refractive index (~ 1.20) due to the nanoporosity, and Lynn and coworkers have extended their reactive LbL system to produce a transparent SLIPS surface as well.⁹³

SUPERHYDROPHILICITY

Superhydrophilic surfaces have potential critical roles in industrially important problems, such as antifogging or to reduce capillary forces that impede fluid flow in confined spaces. The definition of a superhydrophilic surface is an ongoing discussion in the literature with some defining it as a contact angle of less than 5° , and others defining it as a surface with a static water contact angle of less than 10° .³⁹ Furthermore, surface roughness is of importance for superhydrophilic wetting behavior, and accordingly a limitation that only surfaces with a roughness factor of greater than 1 (defined as the ratio of actual area of the surface to its geometric area) should be described as superhydrophilic has been postulated in the literature. When the surface microstructure is the mechanism behind superhydrophilicity, the surface wetting property is a consequence of water penetrating a roughened or porous surface. Another mechanism, and the first reported for fabrication of superhydrophilic surfaces, is based on photoactive materials such as titania that become superhydrophilic after UV irradiation. The physical origin of

superhydrophilicity for these photoactive materials is considered to be either that the UV light catalyzes the degradation of organic surface contamination⁹⁴ or that photogenerated holes trapped on the inorganic surface create oxygen vacancies that then readily absorb water.⁹⁵

Superhydrophilic modifications for plastics have been shown to make antifog surfaces.⁹⁶ LbL is naturally a suitable method to create such coatings. Just as texture is used in the aforementioned examples to create superhydrophobicity, it can be used to create superhydrophilicity from an inherently hydrophilic material. With this strategy, superhydrophilicity is readily achieved from inorganic/organic LbL films, including those with inert particles such as silica or silicates^{97,98} or those incorporating photoactive particles such as titania.^{27,99,100} These superhydrophilic surfaces generated by LbL can be made using solid-, spherical-, or disc-like nanoparticles^{97–99} but more complex geometries such as hollow TiO₂¹⁰⁰ and mesoporous SiO₂ spheres and a number of raspberry- or mulberry-shaped particles have been created by the LbL method to generate superhydrophilic wetting surfaces.^{101–105} For example, He and coworkers made raspberry-shaped particles by the LbL method via two routes.^{103–105} In the first method, raspberry particles are formed by depositing an LbL coating containing silica nanoparticles onto larger silica particles. These raspberry particles are then deposited onto the surface of interest. The second, and more direct, method is to form the raspberry particles directly onto the surface by first depositing the larger particles onto the surface and then depositing the smaller nanoparticles onto the layer of larger particles, using electrostatic interactions to attach the smaller particles to the larger particles. Both of these methods lead to superhydrophilicity. In another example by Su and coworkers,⁶⁵ a superhydrophilic surface is created without inorganic particles by depositing a PEM onto a roughened surface, enhancing its inherent hydrophilicity with roughness. LbL is a versatile approach to generate superhydrophilic surfaces on the basis of the hydrophilic nature of the constituents and the ability to create surface roughness or conformally coat roughness already present on the surface.

EXTRAFUNCTIONALITIES

One of the benefits of the LbL technique is the possibility of incorporating multiple functionalities. Any applications require coatings to be stable and robust, with the wetting properties being durable under conditions of multiple switchable wetting cycles, or possibly under severe mechanical and temperature conditions. Additionally, control of wetting can enable other properties such as antibacterial,^{15,43,45–47} antifogging,⁴⁸ antifrost coatings,⁴⁹ or surfaces that can control condensation.¹⁰⁶ For example, gradients have been shown to be able to control droplet sizes during condensation,¹⁰⁷ and it is possible to create chemical functionality gradients easily on the surface of LbL coatings.^{65,66}

Self-cleaning is a result of the lotus leaf type of superhydrophobicity. Droplets roll off of, as opposed to sliding off of, superhydrophobic surfaces, carrying dust or other debris with them. Superhydrophobic surfaces also perform well in preventing

microbial adhesion. Yin and coworkers^{45,46} incorporated silver nanoparticles into a PEI/PAA LbL matrix^{8,9,46} to further enhance the antibiofouling property of the superhydrophobic coating. This superhydrophobic fluorinated multilayer can efficiently prevent microbes (such as sulfate-reducing bacteria *Desulfovibrio salexigens*, SRB) from adhering over the course of a week. After that, silver ions generated from silver nanoparticle in the matrix are released to kill the SRB. Because of the low permeability of the superhydrophobic outer layers,^{45,46} the release rate of silver ions from the matrix was extremely slow, enabling a long-term antibacterial application.

Antifogging coatings are often made from such superhydrophilic surfaces which promote condensation into a film, creating an optically clear layer of water. Several examples of such films made from LbL systems exist, as described above.^{97–105} However, antifogging surfaces can also be made from surfaces that are both hydrophobic¹⁰⁶ and hygroscopic. Cohen and coworkers have demonstrated so-called zwitter wetting antifogging surfaces made with a hydrophilic PEM topped by a hydrophobic Nafion-containing layer.¹⁰⁸ These films are resistant to liquid water while being able to absorb water vapor, making for antifogging materials that remain dry to the touch. Superhydrophilic LbL surfaces have also been used to enhance cooling on copper surfaces.²⁶

Traditional superhydrophobic surfaces can become unstable under exposure to low-surface-tension liquids (i.e., oil).^{39,90} As surface tension decreases with increasing temperature, further destabilizing the liquid–air interface, it is very challenging to design surfaces that can repel a wide range of liquids over a wide range of temperatures.^{90,109} The previously described omniphobic lubricant-infused SLIPS coating may be able to solve some of these challenges. The lubricant itself has very low freezing temperature, which also helps to postpone the ice forming of the drop on the surface.¹¹⁰ At the same time, due to the lubricant being nonvolatile and stable at a large range of temperature and thus enhance the robustness of the coating.⁹⁰ Moreover, properties have been reported such as the rapid restoration of liquid repellency after physical damage (within 1 s),⁹⁰ function at high pressure (up to 6.85×10^7 Pa)⁹⁰ and high temperature ($\sim 200^\circ\text{C}$),¹¹¹ resistance of bacterial biofouling¹¹² or ice adhesion,¹¹⁰ enhancement of condensation,¹⁰⁶ and switching wettability and transparency in response to mechanical stimuli.³²

It is necessary to develop strategies to overcome practical issues of durability during the coating's lifetime. Both the complex textured morphologies required as well as the chemical functionalization of superhydrophobic surfaces increase their vulnerability to damage, such as bleaching by the sun, scratching, or general wear. This, along with complexity of fabrication, is probably one of the most important reasons that superhydrophobic surfaces have not been more broadly commercialized. One strategy might be to make a tougher or harder coating, and another strategy is to create a self-healing coating.^{49,112,113} In one such example, Sun and coworkers³⁸ reported the use of the facile spray LbL assembly of a mechanically robust and self-healable PFOS-(PAA/PAH-SPEEK)₈₀ coating (Figure 4) by

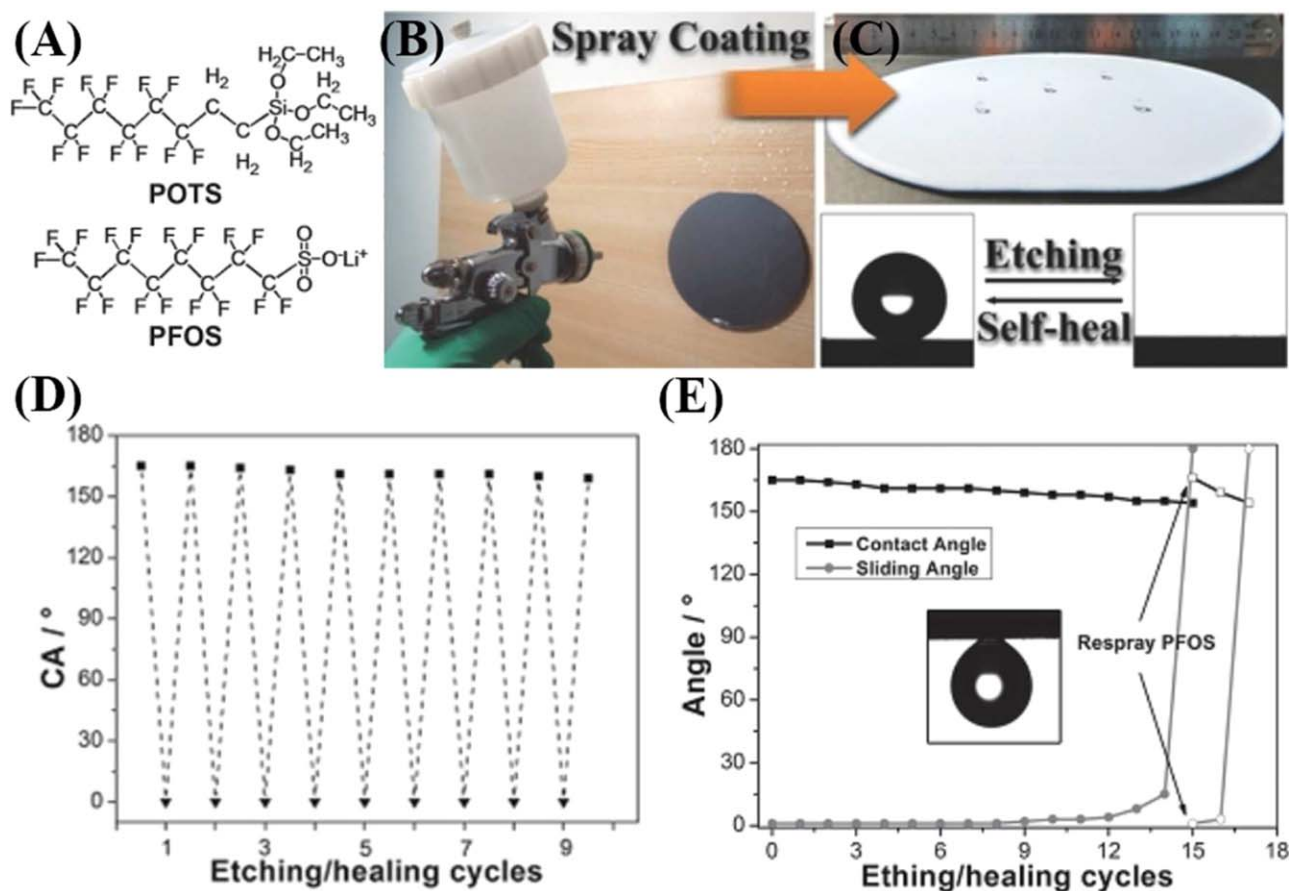


Figure 4. Robust and self-healable superhydrophobic PFOS-(PAA/PAH-SPEEK)₈₀ coating using spraying LbL assembly. (A) Chemical structures of POTS and PFOS, (B) spraying LbL assembly of PFOS-(PAA/PAH-SPEEK)₈₀ coating, (C) shape of water droplet (4 μL) on the PFOS-(PAA/PAH-SPEEK)₈₀ coating under etching and healing cycles, (D) static water contact angle switching between etching (solid triangle) and healing (solid square) cycles. The PFOS-(PAA/PAH-SPEEK)₈₀ coating was etched by O₂ plasma and healed by rehealing agent, PFOS, refilled from porous reservoirs, and (E) static water contact angle (solid square) and sliding angle (solid triangle) of the PFOS-(PAA/PAH-SPEEK)₈₀ coating with different cycles of O₂ plasma etching/healing. Respraying of PFOS solution on the 15th cycle is needed since the water droplet was pinned on the coating (insert image) after 15th etching/healing cycles. (Reproduced from Ref 38, with permission from Wiley). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

spraying PAH-SPEEK [sulfonated poly(ether ether ketone)] complexes, PAA, and a low surface energy healing agent POTS and PFOS. The coating can automatically and repeatedly restore superhydrophobicity after damage by O₂ plasma with 15th etching/healing cycles [Figure 4(D,E)]. The self-healing properties can be easily restore with simple respraying the low surface energy healing agents.

In cases when a superhydrophobic coating is to be applied to a transparent substrate, such as glass or plastic, it may be desirable that the coating be transparent or have antireflection or antiglare properties. However, transparency and superhydrophobicity are often at odds with one another, due to the length scales involved in the superhydrophobic coatings.¹¹⁴ Antireflective coatings may satisfy the transparency issues as they typically have nanoscaled pores and low refractive index,^{105,115} which can even extended to be transparent in the infrared region.⁵¹ Sun and coworkers¹⁰¹ developed a facile way to fabricate highly transparent superhydrophobic coatings using porous silica nanoparticles film with a monolayer of fluoroalkylsilane. The porous silica nanoparticle layer was fabricated by calcination of

a multilayer composed of polyelectrolyte and silica nanoparticles⁹⁷ or silica nanoparticle precursor, such as silicate. An optimized transmittance of 97% was achieved with underlying antireflective nanoporous silica nanoparticle coating topped with a transparent superhydrophobic silica nanoparticle layer.¹⁰⁰ Moreover, the nanoporous silica nanoparticle sublayer can be substituted with a nanoporous PAH/PAA layer yielding a transmittance of 96%.⁵¹ As previously mentioned, Aizenberg and coworkers⁹¹ developed a transparent LbL SLIPS with a similar strategy [Figure 3(B,C)].

SWITCHABLE WETTABILITY

Intelligent surfaces with reversible and switchable wetting properties are of great importance for application in areas such as biological interfaces, separators, microfluidic devices, tunable optical lenses, and lab-on chip systems. For these switchable surfaces, dramatic changes in surface energy occur under external stimuli, such as light, temperature, solvent, electrical potential, pH, ionic strength, and exchange of counterions.^{30,116–120} The surface of PEM films is by nature mutable and dynamic.

The conformation, ionization, and construction of charged polyelectrolyte on the surface can be easily tuned by pH, electrical potential, ionic strength, and surfactant of the surrounding environment,^{1,3,8,19,67} all of which can be effective external stimuli to control surface wettability.

Incorporation of amphiphilic surfactant into PEMs is one approach to change the surface chemistry and expand the functionality of PEMs made from the standard library of commercially available polyelectrolytes. Surfactants are able to diffuse and swell into PEMs.⁸ During this interdiffusion process, complexes between polyelectrolytes and surfactants can be formed through electrostatic or secondary interactions, displacing small counterions in the multilayer or even the ion pairs formed between polyelectrolytes. The charged surfactant is able to become incorporated into the multilayer adding new functionality, such as hydrophobicity. Moreover, this newly incorporated property can be tuned. The surfactant can be incorporated in such a fashion as to create a gradient or switchable wetting (erasable-rewritable) with controlling this interdiffusion procedure. There are some reports of using the counterion exchange from small counterions to larger surfactant molecules on the top surface of a PEM surface in order to modify the wettability.^{55,65,117–120} Johal and coworkers¹²⁰ showed that the adsorption of an anionic surfactant, sodium dodecyl sulfate (SDS), onto the outer layer can be used to fine-tune the wettability. Cho and coworkers⁵⁵ reported the intelligent polyelectrolyte copolymer [poly(2-methacryloyloxy)ethyltrimethylammonium chloride-*co*-trifluoroethyl methacrylate] [poly-(METAC-*co*-TMA)] brush surface with dynamically tunable wettability by direct counterion exchange, reversible switching between superhydrophobicity ($171^\circ \pm 3^\circ$) and superhydrophilicity ($<5^\circ$). Su and coworkers^{54,58} fabricated an erasable-rewritable wettability gradient between superhydrophobicity to superhydrophilicity via counterion exchange of the PEM film with PFO⁻. With fluorinated surfactant (ammonium perfluorooctanoate, APFO) co-assembly, a gradient of wettability from hydrophilic to hydrophobic can be achieved and modulated through simply changing the surfactant concentration of assemble solutions, which has been demonstrated by Zacharia and coworkers.⁶⁶

Zhou and coworkers⁵⁶ further extended the counterion exchange concept, using the PEM-ion exchange system^{54,65} reported by Su and coworkers on cotton fabrics, and demonstrated that it not only has switchable hydrophobicity but also switchable oleophobicity due to the re-entrant surface texture of cotton fabrics. Actually this switchable wetting for both oil and water is also possible for a textured surface with a carefully designed texture, such as a nanoflake aluminum surface.⁷⁹ With a similar polyelectrolyte deposition and ion exchange procedure, a surface was made with a $\sim 160^\circ$ contact angle for low surface tension liquids such as hexadecane. This property can be erased and rewritten from superoleophobicity to superoleophilicity by a simple counterion exchange.⁵⁷ Moreover, this switchable wetting is stable not only in air, but remained constant in seawater simulant (NaCl: 2.6726 g; MgCl₂: 0.2260 g; MgSO₄: 0.3248 g; CaCl₂: 0.1153 g; H₂O: 100 mL) and can be switched back to superoleophobicity in air by exchanging the counterion with PFO⁻. Instead of an LbL coating, Wang and coworkers⁵⁹ graft

polycation, poly[2-(methacryloyloxy) ethyltrimethyl ammonium chloride] (PMETAC) onto the cotton fiber surface via surface-initiated atom transfer radical polymerization (SI-ATRP). When exchanging the counterions between PFO⁻ and thiocyanate (SCN⁻), the surface reversibly switched from superhydrophobic ($\sim 154^\circ$) to superhydrophilic ($<5^\circ$). Moreover, Cho and coworkers⁶⁰ produced a “smart fabric” via electrospinning the polyelectrolyte copolymer [poly(METAC-*co*-3-trimethoxysilyl)propylmethacrylate] [poly(METAC-*co*-TSPM)] to create a nanofibrous fabric template. Each polyelectrolyte copolymer nanofiber can exchange different counterions with various hydration energies. This nanoscaled surface texture also enabled switchable wetting for both water and oil.

Polyelectrolyte coil conformations are known to be sensitive to both the pH and ionic strength of assembly solution as well as the postimmersion environment.^{1,3,8,52} These can in turn play a role in determining whether a larger proportion of functional groups or the polymer backbone is presented at the polymer/air interface. Wettability can be tuned by pH value of the polyelectrolyte assembly solutions when using weak polyelectrolytes, as the charge density of the polyelectrolyte is pH dependent.¹¹⁹ This responsiveness of polyelectrolytes to different conditions of pH is a way to create surfaces capable of switching properties. However, under extreme acidic or basic pH conditions, weak polyelectrolyte assemblies held together via electrostatic interactions can decompose or reorganize to form porous structures.^{8,17,19,52} If this kind of response is not desired, the films should be at least partially covalently crosslinked. Jiang and coworkers¹¹⁶ reported a bell-shaped superhydrophilic-superhydrophobic-superhydrophilic double transformation in response to the increase in the pH value of surrounding solution by covalent surface modification of alkyl, amino, and carboxylic acid groups. Sun and coworkers⁶² grafted the thermal- and pH-responsive poly(*N*-isopropylacrylamide-*co*-acrylic acid) [P(NIPAAm-*co*-AAc)] copolymer as well as the low surface energy small molecule heptadecafluorodecyltrimethoxysilane (FAS) on a nanopatterned silicone surface, which demonstrated switching of adhesive properties to water (superhydrophobic roll-off/sticky property) triggered by temperature and pH. Sukhishvili and coworkers⁶³ partially crosslinked poly(2-alkylacrylic acid) hydrogel, which is able to undergo a reversible collapse (hydrophobic)/dissolution (hydrophilic) transition as a function of pH.

DROPLET MOBILITY GUIDING

Guiding the motion of a droplet, especially the water droplet, is another kind of intelligent surface, which goes well beyond the superwettability and keeping the surface clean. It controls the liquid flows like the tear film on eyes, and tuned by both the property of fluid and the interacted surface.¹²⁰ This kind of intelligent surface has the potential application in water harvesting, controlled drug release, open-air microchannel device, and lab-on-chip device. Taking inspiration again from nature, one can consider the Namib beetle which harvests water from the low humidity atmosphere via its hydrophilic/hydrophobic patterned surface of the wings to collect the drinking water from fog-laden wind.¹²¹ Droplets condense in the hydrophilic domains and coalesce into larger drops. When the weight of a growing droplet is

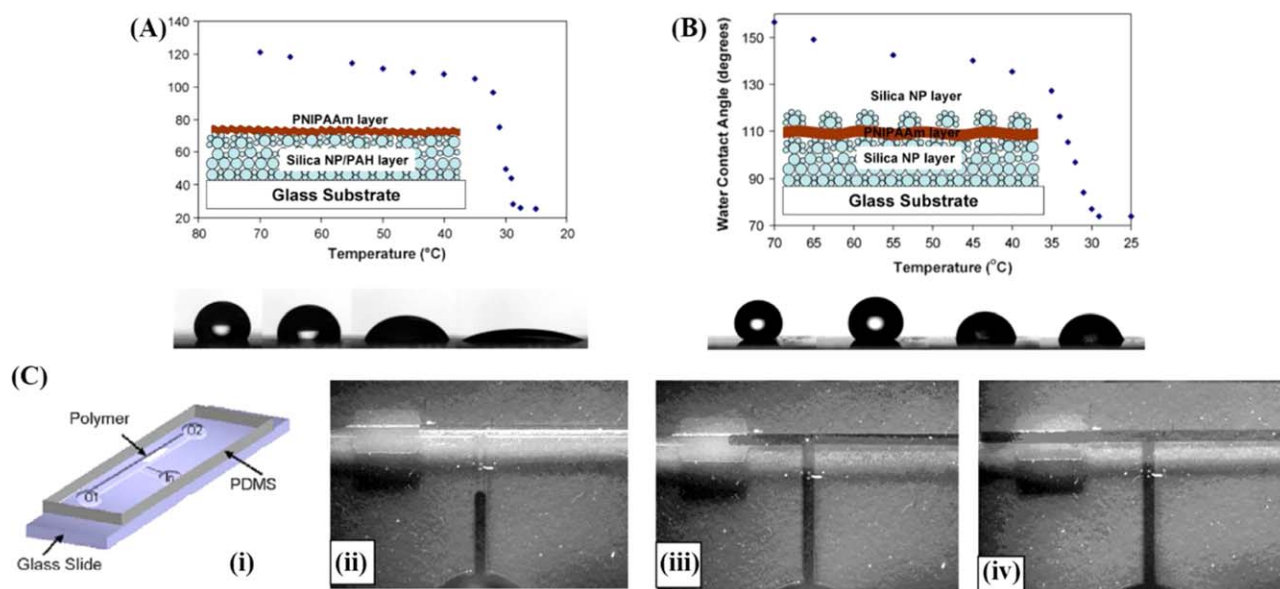


Figure 5. The thermally stimulated switchable superhydrophobic/hydrophilic surface for thermal valve. (A) The change of water contact angle from hydrophilic to hydrophobic with increasing the temperature. (B) The change of water contact angle from superhydrophilic to hydrophobic with increasing the temperature by the introduction for nanoscaled roughness. (C) The water flow in T-junction microfluidic channel with a thermal valve. (i) The schematic illustration; (ii) dyed water approaches to T-junction; (iii) stops at superhydrophobic patch at elevated temperature, and (iv) passes through the hydrophilic patch at room temperature. (Reproduced from Ref 122, with permission from Elsevier). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sufficient to overcome the binding forces of the hydrophilic region, it detaches and rolls down the superhydrophobic surface to the beetle's mouth via gravity. Rubner and coworkers⁶⁴ demonstrate the mimic structure via selective deposition of PEM film (PAH/PAA/silica nanoparticle) to create a surface with an extreme contrast in hydrophilicity/hydrophobicity.

The ability to tune a textured surface from superhydrophobic to superhydrophilic (switchable wetting) creates many possibilities. Water drops can roll off from areas of water sliding to areas of water pinning where they remain pinned and coalesce into larger drops.^{27,65,114} A wettability gradient ensures the motion of water droplets from superhydrophobic regions to superhydrophilic regions. Su and coworkers⁶⁵ reported a gradient of wettability from $\sim 153^\circ$ to $<5^\circ$ in water contact angle via counterion exchange. The water contact angle can be simply tuned via PFO⁻ ion exchanging time.^{65,120}

Switchable superhydrophobicity can be used to create a valve in a microchannel.¹²² When water flows through the hydrophilic microchannel comes to the superhydrophobic portion of the channel, the water flow will stop, repelled by the superhydrophobic patch. Zhai and coworkers¹²² built a PEM of PAH and silica with controlled thickness as well as roughness. After functionalization with a layer of temperature-sensitive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel and a monolayer of perfluorosilane, the coating in microfluidic channel will be hydrophilic. The hydrophobicity/hydrophilicity can be tuned via temperature (Figure 5). The extra nanoscaled roughness will cause the hydrophobic surface to become a superhydrophobic region, enlarging the differences in wettability. When the coating applied on the T-junction microfluidic channel, it can stop the

water flow at the superhydrophobic patch at high temperature. Once the temperature decreases to room temperature, the surface becomes hydrophilic and allows the water flow through this patch [Figure 5(C)].

CONCLUSION AND FUTURE PERSPECTIVE

The creation of superhydrophobic materials began with the replication of natural surfaces, but it has been extended beyond simple biomimicry to created surfaces with properties that are different than or even superior to natural surfaces. The control of surface wetting is a multidisciplinary field overlapping with surface chemistry, physics, nanomaterials, biosurface and interface, mechanics, and so on. This review reports the recent progress of control over different types of wettability, including the surfaces that are super-repellant or superwetting to various liquids, anti-icing, or anti-ogging coatings, but also intelligent surfaces with a range of functionality such as reversible/switchable wetting or droplet mobility guiding. The focus here is on coatings based on the LbL assembly of water-soluble polymers or colloidal dispersions, which are often hydrophilic materials. Such coatings can become superwetting via introducing roughness and/or low surface energy layers in multiple ways. Moreover, the coating thickness and composition is controlled quite precisely by the LbL technique, which allows for creating "intelligent" systems, for example, modulating wettability and advanced functionalities such as water flow guidance. LbL can be used to create nearly any surface texture, making it a natural choice for the creation of surfaces with special wettability. However, there are still several challenges facing the fabrication of superwetting coatings in general and more specifically via LbL.

Although spray LbL dramatically decreases assembly times over dipping, multiple steps are still required to obtain the coatings with desirable properties. How to develop such coating with even simpler processes remains a challenge for the LbL community. Such factors will become extremely important when scaling up the coating fabrication. One possible answer is the simple spraying of a polyelectrolyte complex instead of LbL assembly of multiple polyelectrolytes. Optical properties of these coatings are a further area of investigation. Another important challenge that applies to all superhydrophobic surfaces not only those made by LbL is the application of robust coatings to flexible and complex substrates, such as fabrics. Many of the coatings mentioned in this review are mechanically robust when coated on flat surfaces, such as glass, plastic, and metals. A coating applied to complex surfaces such as fabrics must be able to withstand a number of mechanical and chemical stresses such as twisting, washing, and folding. A successful coating for this application will also require elasticity. A final important consideration for this field more generally is the use of perfluorinated acids, which can be environmentally persistent and even bioaccumulative.¹²³ Optimizing surface texture, an advantage with LbL, might be able to overcome this problem.

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REFERENCES

1. Decher, G.; Schlenoff, J. B. *Multilayer Thin Film: Sequential Assembly of Nanocomposite Materials*, 2nd ed.; Wiley-VCH: Weinheim, Germany, **2012**.
2. Lutkenhaus, J. L.; Hammond, P. T. *Soft Matter* **2007**, *3*, 804.
3. Borges, J.; Mano, F. J. *Chem. Rev.* **2014**, *114*, 8883.
4. Kozlovskaya, V.; Kharlampieva, E.; Erel, I.; Sukhishvili, S. A. *Soft Matter* **2009**, *5*, 4077.
5. Kotov, N. A. *Nanostruct. Mater.* **1999**, *12*, 789.
6. Wang, Y.; Angelatos, A. S.; Caruso, F. *Chem. Mater.* **2008**, *20*, 848.
7. Mentbayeva, A.; Ospanova, A.; Tashmuhambetova, Z.; Sokolova, V.; Sukhishvili, S. *Langmuir* **2012**, *28*, 11948.
8. Huang, X.; Schubert, A. B.; Chrisman, J. D.; Zacharia, N. S. *Langmuir* **2013**, *29*, 12959.
9. Huang, X.; Zacharia, N. S. *ACS Macro Lett.* **2014**, *3*, 1092.
10. Huang, X.; Bolen, M. J.; Zacharia, N. S. *Phys. Chem. Chem. Phys.* **2014**, *16*, 10267.
11. Quinn, J. F.; Johnston, A. P. R.; Such, G. K.; Zelikin, A. N.; Caruso, F. *Chem. Soc. Rev.* **2007**, *36*, 707.
12. Ariga, K.; Hill, J. P.; Ji, Q. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2319.
13. Ariga, K.; Yamauchi, Y.; Rydzek, G.; Ji, Q.; Yonamine, Y.; Wu, K. C. W.; Hill, J. P. *Chem. Lett.* **2014**, *43*, 36.
14. Wohl, B. M.; Engbersen, J. F. J. *J. Control. Release* **2012**, *158*, 2.
15. Dvoracek, C. M.; Sukhonosova, G.; Benedik, M. J.; Grunlan, J. C. *Langmuir* **2009**, *25*, 10322.
16. Wang, X.; Liu, F.; Zheng, X.; Sun, J. *Angew. Chem. Int. Ed.* **2011**, *50*, 11378.
17. Shchukin, D. G.; Mohwald, H. *Small* **2007**, *3*, 926.
18. Zhai, L.; Cebeci, F. C.; Cohen, R. E.; Rubner, M. F. *Nano Lett.* **2004**, *4*, 1349.
19. Huang, X.; Chrisman, J. D.; Zacharia, N. S. *ACS Macro Lett.* **2013**, *2*, 826.
20. Feng, X.; Jiang, L. *Adv. Mater.* **2006**, *18*, 3063.
21. Zhang, X.; Shi, F.; Niu, J.; Jiang, Y.; Wang, Z. *J. Mater. Chem.* **2008**, *18*, 621.
22. Liu, M.; Wang, S.; Jiang, L. *MRS Bull.* **2013**, *38*, 375.
23. Lee, C.; Choi, C. H.; Kim, C. J. *Phys. Rev. Lett.* **2008**, *101*, 064501.
24. Srinivasan, S.; Choi, W.; Park, K. C.; Chhatre, S. S.; Cohen, R. E.; McKinley, G. H. *Soft Matter* **2013**, *9*, 5691.
25. Paxson, A. T.; Yagüe, J. L.; Gleason, K. K.; Varanasi, K. K. *Adv. Mater.* **2014**, *26*, 418.
26. Tian, Y.; Su, B.; Jiang, L. *Adv. Mater.* **2014**, *26*, 6872.
27. McDonald, B. T.; Cui, T. H. *J. Colloid Interface Sci.* **2011**, *354*, 1.
28. Adera, S.; Raj, R.; Enright, R.; Wang, E. N. *Nat. Commun.* **2013**, *4*, 2518.
29. Wang, F. J.; Lei, S.; Ou, J. F.; Xue, M. S.; Li, W. *Appl. Surf. Sci.* **2013**, *276*, 397.
30. Liu, X.; Liang, Y.; Zhou, F.; Liu, W. *Soft Matter* **2012**, *8*, 2070.
31. Xin, B.; Hao, J. *Chem. Soc. Rev.* **2010**, *39*, 769.
32. Nosonovsky, M. *Nature* **2011**, *477*, 412.
33. Kim, P.; Kreder, M. J.; Alvarenga, J.; Aizenberg, J. *Nano Lett.* **2013**, *13*, 1793.
34. Shi, F.; Wang, Z.; Zhang, X. *Adv. Mater.* **2005**, *17*, 1005.
35. Anand, S.; Paxson, A. T.; Dhiman, R.; Smith, J. D.; Varanasi, K. K. *ACS Nano* **2012**, *6*, 10122.
36. Vogel, N.; Belisle, R. A.; Hatton, B.; Wong, T. S.; Aizenberg, J. *Nat. Commun.* **2013**, *4*, 2167.
37. Yao, X.; Hu, Y.; Grinthal, A.; Wong, T. S.; Mahadevan, L.; Aizenberg, J. *Nat. Mater.* **2013**, *12*, 529.
38. Li, Y.; Chen, S.; Wu, M.; Sun, J. *Adv. Mater.* **2014**, *26*, 3344.
39. Tettey, K. E.; Dafinone, M. I.; Lee, D. *Mater. Express* **2011**, *1*, 89.
40. Wong, T. S.; Sun, T.; Feng, L.; Aizenberg, J. *MRS Bull.* **2013**, *38*, 366.
41. Onda, T.; Shibuichi, S.; Satoh, N.; Tsujii, K. *Langmuir* **1996**, *12*, 2125.
42. Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Oner, D.; Youngblood, J.; McCarthy, T. J. *Langmuir* **1999**, *15*, 3395.
43. Oner, D.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7777.
44. Feng, L.; Zhang, Y. A.; Xi, J. M.; Zhu, Y.; Wang, N.; Xia, F.; Jiang, L. *Langmuir* **2008**, *24*, 4114.

45. Liu, T.; Yin, B.; He, T.; Guo, N.; Dong, L.; Yin, Y. *ACS Appl. Mater. Interface* **2012**, *4*, 4683.
46. Yin, B.; Liu, T.; Yin, Y. *Langmuir* **2012**, *28*, 17019.
47. Shen, L.; Wang, B.; Wang, J.; Fu, J.; Picart, C.; Ji, J. *ACS Appl. Mater. Interfaces* **2012**, *4*, 4476.
48. Liu, X.; Du, X.; He, J. *ChemPhysChem* **2008**, *9*, 305.
49. Guo, P.; Zheng, Y.; Wen, M.; Song, C.; Lin, Y.; Jiang, L. *Adv. Mater.* **2012**, *24*, 2642.
50. Manna, U.; Lynn, D. M. *Adv. Mater.* **2013**, *25*, 5104.
51. Zhang, L.; Li, Y.; Sun, J.; Shen, J. *J. Colloid Interface Sci.* **2008**, *319*, 302.
52. Hiller, J.; Mendesohn, J. D.; Rubner, M. F. *Nat. Mater.* **2002**, *1*, 59.
53. Hua, Z.; Yang, J.; Wang, T.; Liu, G.; Zhang, G. *Langmuir* **2013**, *29*, 10307.
54. Wang, L.; Lin, Y.; Su, Z. *Soft Matter* **2009**, *5*, 2072.
55. Lim, H. S.; Lee, S. G.; Lee, D. H.; Lee, D. Y.; Lee, S.; Cho, K. *Adv. Mater.* **2008**, *20*, 4438.
56. Yang, J.; Zhang, Z.; Men, X.; Xu, X.; Zhu, X.; Zhou, X. *Langmuir* **2011**, *27*, 7357.
57. Yang, J.; Zhang, Z.; Men, X.; Xu, X.; Zhu, X.; Zhou, X.; Xue, Q. *J. Colloid Interface Sci.* **2012**, *366*, 191.
58. Zhang, G.; Zhang, X.; Huang, Y.; Su, Z. *ACS Appl. Mater. Interfaces* **2013**, *5*, 6400.
59. Jiang, C.; Wang, Q.; Wang, T. *New J. Chem.* **2012**, *36*, 1641.
60. Lee, C. H.; Kang, S. K.; Lim, J. A.; Kwark, Y. J.; Lim, H. S.; Kim, J.; Cho, J. H. *J. Mater. Chem.* **2012**, *22*, 14656.
61. Motornov, M.; Tam, T. K.; Pita, M.; Tokarev, I.; Katz, E.; Minko, S. *Nanotechnology* **2009**, *20*, 434006.
62. Cheng, Z.; Lai, H.; Du, M.; Zhu, S.; Zhang, N.; Sun, K. *Soft Matter* **2012**, *8*, 9635.
63. Lu, Y.; Sarshar, M. A.; Du, K.; Chou, T.; Choi, C. H.; Sukhishvili, S. A. *ACS Appl. Mater. Interfaces* **2013**, *5*, 12617.
64. Zhai, L.; Berg, M. C.; Cebeci, F. C.; Kim, Y.; Milwid, J. M.; Rubner, M. F.; Cohen, R. E. *Nano Lett.* **2006**, *6*, 1213.
65. Wang, L.; Peng, B.; Su, Z. *Langmuir* **2010**, *26*, 12203.
66. Huang, X.; Zacharia, N. S. *Soft Matter* **2013**, *9*, 7735.
67. Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* **1998**, *31*, 4309.
68. Barthlott, W.; Neinhuis, C. *Planta* **1997**, *202*, 1.
69. Jung, Y. C.; Bhushan, B. *Langmuir* **2009**, *25*, 14165.
70. Soeno, T.; Inokuchi, K.; Shiratori, S. *Trans. Mater. Res. Soc. Jpn.* **2003**, *28*, 1207.
71. Sun, W.; Shen, L.; Wang, J.; Fu, K.; Ji, J. *Langmuir* **2010**, *26*, 14236.
72. Jindasuwan, S.; Nimittrakoolchai, O.; Sujaridworakun, P.; Jinawath, S.; Supothina, S. *Thin Solid Films* **2009**, *517*, 5001.
73. Zhao, Y.; Tang, Y.; Wang, X.; Lin, T. *Appl. Surf. Sci.* **2010**, *256*, 6736.
74. Du, X.; Liu, X.; Chen, H.; He, J. *J. Phys. Chem. C* **2009**, *113*, 9063.
75. Zhang, L.; Sun, J. *Macromolecules* **2010**, *43*, 2413.
76. Liu, X.; Dai, B.; Zhou, L.; Sun, J. *J. Mater. Chem.* **2009**, *19*, 497.
77. Buck, M. E.; Schwartz, S. C.; Lynn, D. M. *Chem. Mater.* **2010**, *22*, 6319.
78. Broderick, A. H.; Manna, U.; Lynn, D. M. *Chem. Mater.* **2012**, *24*, 1786.
79. Kim, Y. H.; Lee, Y. M.; Lee, J. Y.; Ko, M. J.; Yoo, P. J. *ACS Nano* **2012**, *6*, 1082.
80. Lai, Y. K.; Gao, X. F.; Zhuang, H. F.; Huang, J. Y.; Lin, C. J.; Jiang, L. *Adv. Mater.* **2009**, *21*, 3799.
81. Extrand, C. W. *Langmuir* **2002**, *18*, 7991.
82. Wang, L.; Wei, J.; Su, Z. *Langmuir* **2011**, *27*, 15299.
83. Huang, H. C.; Zacharia, N. S. *Langmuir* **2015**, *31*, 714.
84. Xu, L. P.; Peng, J.; Liu, Y.; Wen, Y.; Zhang, X.; Jiang, L.; Wang, S. *ACS Nano* **2013**, *7*, 5077.
85. Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; Mckinley, G. H.; Cohen, R. E. *Science* **2007**, *318*, 1618.
86. Kota, A. K.; Choi, W.; Tuteja, A. *MRS Bull.* **2013**, *38*, 383.
87. Choi, W.; Tuteja, A.; Chhatre, S.; Mabry, J. M.; Cohen, R. E.; McKinley, G. H. *Adv. Mater.* **2009**, *21*, 2190.
88. Aulin, C.; Yun, S. H.; Wagberg, L.; Lindstrom, T. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2443.
89. Brown, P. S.; Bhushan, B. *Sci. Rep.* **2015**, *5*, 8701.
90. Wong, T. S.; Kang, S. H.; Tang, S. K. Y.; Smythe, E. J.; Hatton, B. D.; Crinthal, A.; Aizenberg, J. *Nature* **2011**, *477*, 443.
91. Sunny, S.; Vogel, N.; Howell, C.; Vu, T. L.; Aizenberg, J. *Adv. Funct. Mater.* **2014**, *24*, 6658.
92. Manabe, K.; Nishizawa, S.; Kyung, K. H.; Shiratori, S. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13985.
93. Manna, U.; Lynn, D. M. *Adv. Mater.* **2015**, *27*, 3007.
94. Fujishiryma, A.; Zhang, X. T.; Tryk, D. A. *Surf. Sci. Rep.* **2008**, *63*, 515.
95. Carp, O.; Huisman, C. L.; Reller, A. *Prog. Solid State Chem.* **2004**, *32*, 33.
96. DiMundo, R.; d'Agostino, R.; Palumbo, F. *ACS Appl. Mater. Interfaces* **2014**, *6*, 17059.
97. Chen, P.; Hu, Y.; Wei, C. *Appl. Surf. Sci.* **2012**, *258*, 4334.
98. Zhang, L.; Li, Y.; Sun, J.; Shen, J. *Langmuir* **2008**, *24*, 10851.
99. Eita, M.; Wågberg, L.; Muhammed, M. *J. Phys. Chem. C* **2012**, *116*, 4621.
100. Peng, B.; Tan, L.; Chen, D.; Meng, X.; Tang, F. *ACS Appl. Mater. Interfaces* **2012**, *4*, 96.
101. Zhang, L.; Qiao, Z. A.; Zheng, M.; Huo, Q.; Sun, J. *J. Mater. Chem.* **2010**, *20*, 6125.
102. Du, X.; Li, X.; He, J. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2365.
103. Liu, X.; He, J. *J. Colloid Interface Sci.* **2007**, *314*, 341.
104. Du, X.; Liu, X.; Chen, H.; He, J. *J. Phys. Chem. C* **2009**, *113*, 9063.

105. Li, X.; He, J. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2204.
106. Anand, S.; Paxson, A. T.; Dhiman, R.; Smith, J. D.; Varanasi, K. K. *ACS Nano* **2012**, *6*, 10122.
107. Macner, A. M.; Daniel, S.; Steen, P. H. *Langmuir* **2014**, *30*, 1788.
108. Lee, H.; Giibert, J. B.; Angile, F. E.; Yang, R.; Lee, D.; Rubner, M. F.; Cohen, R. E. *ACS Appl. Mater. Interfaces* **2015**, *7*, 1004.
109. Liu, Y.; Chen, X.; Xin, J. H. *J. Mater. Chem.* **2009**, *19*, 5602.
110. Kim, P.; Wong, T. S.; Alvarenga, J.; Kreder, M. J.; Adorno-Martinez, W. E.; Aizenberg, J. *ACS Nano* **2012**, *6*, 6569.
111. Daniel, D.; Mankin, M. N.; Belisle, R. A.; Wong, T. S.; Aizenberg, J. *Appl. Phys. Lett.* **2013**, *102*, 231603.
112. Epstein, A. K.; Wong, T. S.; Belisle, R. A.; Boggs, E. M.; Aizenberg, J. *Proc. Natl. Acad. Sci.* **2012**, *109*, 13182.
113. Verho, T.; Bower, C.; Andrew, P.; Franssila, S.; Ikkala, O.; Ras, R. H. *Adv. Mater.* **2011**, *23*, 673.
114. Deng, X.; Mammen, L.; Butt, H. J.; Vollmer, D. *Science* **2012**, *335*, 67.
115. Li, Y.; Liu, F.; Sun, J. *Chem. Commun.* **2009**, *19*, 2730.
116. Chen, T.; Ferris, R.; Zhang, J.; Ducker, R.; Zauscher, S. *Prog. Polym. Sci.* **2010**, *35*, 94.
117. Cheng, M.; Liu, Q.; Ju, G.; Zhang, Y.; Jiang, L.; Shi, F. *Adv. Mater.* **2014**, *26*, 306.
118. Liu, X.; Ye, Q.; Song, X.; Zhu, Y.; Gao, X.; Liang, Y.; Zhou, F. *Soft Matter* **2011**, *7*, 515.
119. Johal, M. S.; Chiarelli, P. A. *Soft Matter* **2007**, *3*, 34.
120. El-Khoury, R. J.; Johal, M. S. *Langmuir* **2003**, *19*, 4880.
121. Parker, A. R.; Lawrence, C. R. *Nature* **2001**, *414*, 33.
122. Chunder, A.; Etcheverry, K.; Londe, G.; Cho, H. J.; Zhai, L. *Colloids Surf. A: Physicochem. Eng. Aspects* **2009**, *333*, 187.
123. Conder, J. M.; Hoke, R. A.; de Wolf, W.; Russell, M. H.; Buck, R. C. *Environ. Sci. Technol.* **2008**, *42*, 995.