

How Does Chemistry Influence Liquid Wettability on Liquid-Infused Porous Surface?

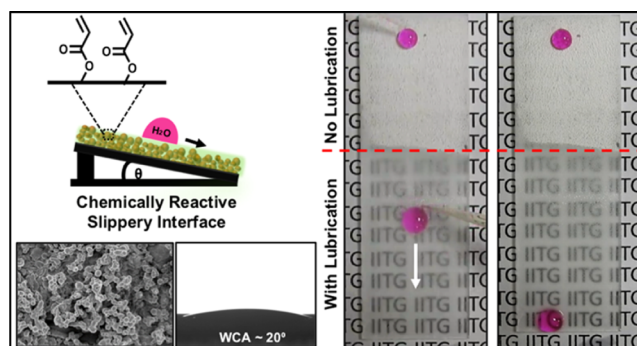
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ABSTRACT: Design of Nepenthes pitcher inspired slippery liquid infused porous surface (SLIPS) appeared as an important avenue for various potential and practically relevant applications. In general, hydrophobic base layers were infused with selected liquid lubricants for developing chemically inert SLIPS. Here, in this current study, an inherently hydrophilic (soaked beaded water droplet with $\sim 20^\circ$ within a couple of minutes), porous and thick (above $200\ \mu\text{m}$) polymeric coating, loaded with readily chemically reactive acrylate moieties yielded a chemically reactive SLIPS, where residual acrylate groups in the synthesized hydrophilic and porous interface rendered stability to the infused lubricants. The chemically reactive SLIPS is capable of reacting with the solution of primary amine containing nucleophiles in organic solvent through 1,4 conjugate addition reaction, both in the presence (referred as “in situ” modification) and absence (denoted as pre modification) of lubricated phase in the porous polymeric coating. Such amine reactive SLIPS was further extended to (1) examining the impact of different chemical modifications on the performance of SLIPS and (2) developing a spatially selective and “in situ” postmodification with primary amine containing nucleophiles through 1,4 conjugate addition reaction. Moreover, the chemically reactive SLIPS was capable of sustaining various physical abrasions and prolonged (minimum 10 days) exposure to complex and harsh aqueous phases, where infused lubricants protect the residual acrylate groups from harsh aqueous exposures. Such, principle will be certainly useful for spatially selective covalent immobilization of water insoluble functional molecules/polymers directly from organic solvents, which would be of potential interest for various applied and fundamental contexts.

KEYWORDS: slippery interface, polymeric coatings, in situ modification, bio inspired wettability, chemically reactive

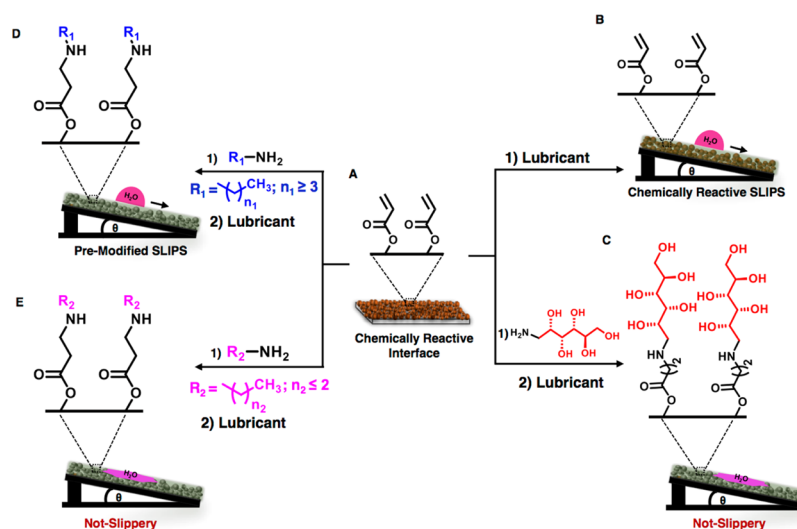
1. INTRODUCTION

The modulation of essential topography and appropriate chemistry remained a primary basis behind developing various functional and smart interfaces.¹⁻⁴ In 2011, Aizenberg and co workers introduced a Nepenthes pitcher inspired slippery liquid infused porous surface (SLIPS) through the strategic use of a porous fluorinated matrix and fluorine based liquid lubricant, where the chemical compatibility between the infused lubricant and the matrix is hypothesized to be a key and essential parameter for achieving a nonadhesive slippery interface for probe liquids.⁵ Since then, this hypothesis has been followed for synthesizing a bioinspired SLIPS, where hydrophilic hierarchically featured/porous interfaces (denoted as base layer) are routinely hydrophobized with long tail hydrocarbons, aromatic groups, fluorinated small molecules, and so forth, following chemical and physical deposition processes, prior to infusing with selected fluorinated/non fluorinated lubricants.⁶⁻²⁹ In another approach, an inherent hydrophobic base layers were developed by associating hydrophobic polymers or nanomaterials to prepare advanced and different stimuli responsive SLIPS³⁰⁻⁴³ for printing



assisted functionalization,³⁰ programable droplet manipulation,^{31,32} developing patterned interface,³³ controlled switching of liquid wettability,³⁴⁻³⁷ controlled transfer of gas, and so on.³⁸⁻⁴³ However, eventually, chemically inert and highly hydrophobic interfaces were mostly used in the reported SLIPS. Is this lubrication of hydrophobic and inert base layer a necessary requirement to achieve SLIPS? As per our knowledge, there is no report in the literature to address this fundamental and important concern on SLIPS that have immense prospects for widespread practically relevant applications including tissue engineering, gas and liquid transport, anticorrosion, water harvesting, drug delivery, and so forth.⁵⁻⁴³ To address this important aspect of the biomimicked interface, a design of a readily chemically

Scheme 1. (A) Schematic Representation of Chemically Reactive Porous Polymeric Coating that Instantly Became SLIPS (B)—after Lubrication with Silicone Oil; Whereas, the Same Polymeric Coating Utterly Fail To Display Slippery Behavior after Post Chemical Modification with Glucamine (C) Through 1,4 Conjugate Addition Reaction. Nevertheless, the Chemically Reactive Polymeric Coating Remained Efficient To Display SLIPS after Post Covalent Modification with Higher Analogues of Butylamine (D), Whereas No Slippery Property Was Noticed for Polymeric Coating That Was Treated with Butylamine and Its Lower Analogue (E)



reactive, hydrophilic, and porous interface is essential, where the chemically reactive porous interface would allow systematic post covalent modification with small molecules having different hydrocarbon tail length. Routinely, either highly hydrophobic or superhydrophobic base layers were developed for stabilizing infused lubricants in the porous interface of the SLIPS. However, the minimal chemical requirements have not been systematically examined due to the lack of suitable substrates, with porosity, hydrophilicity, and ready chemical reactivity. In the past, few chemically reactive and porous coatings were introduced in the literature, but most of them were inherently superhydrophobic and were generally utilized in synthesizing interfaces displaying patterned extreme water wettabilities.^{44–46} The embedded extreme water repellency in the reported chemically reactive bioinspired coatings^{44–46} makes such an interface inappropriate for evaluating the minimal and necessary chemical requirement that is required for stabilizing the lubricant phase in the liquid infused porous interfaces. Even though, both the topography and chemistry were hypothesized to be crucial fundamentals behind designing the bioinspired SLIPS.⁵ Only the role of topography on the bioinspired SLIPS is examined thoroughly, where it was proven that the hierarchical topography is not an essential criteria for synthesizing a liquid infused slippery interface, even interfaces with only nanometer scale features are also capable of displaying slippery property.^{47,48} However, progress on designing appropriate experiments capable of evaluating the exact role of chemistry for designing the SLIPS is few, likely due to the challenge in synthesizing hydrophilic yet chemically reactive porous interfaces.

Besides the above mentioned challenge, recently, few porous polymeric coatings were spatially modulated with hydrophobic and hydrophilic chemical moieties for developing interfaces with patterned wettability.^{49–52} After infusion with selected liquid lubricants, the portion of the porous interface selectively modified with long tail hydrocarbon/fluorinated molecules provided SLIPS, and the area of coating modified with a

hydrophilic moiety failed to display such bioinspired property.^{49–52} This study strongly suggested that the macro scale perturbation in chemistry is likely to scarify the slippery property in SLIPS. Even though the mobility of lubricants in SLIPS has the ability to self heal abrasions in the order of μm scale,⁵ but most of the reported SLIPS that are developed based on the postmodification on the top of hydrophilic hierarchical features (base layer) with the thin layer (in the order of nm) of hydrophobic coating^{6–25} are fundamentally inappropriate to tolerate macroscale (in order of few cm and more) physical abrasion, likely due to the damage of the appropriate chemical makeup that is mostly optimized only over few nanometers across the thickness of the reported SLIPS.^{6–25} Thus, any macroscale (in order of mm/cm) physical abrasions on the conventional design of the SLIPS is expected to expose the hydrophilic interior, misbalancing the chemical compatibility between the featured interface and infused lubricant, and eventually, most of the reported SLIPS are therefore unlikely to perform in practically relevant different physical abrasive settings. However, recently, self healing SLIPS were developed by strategic association of supramolecular polymers, and such designs were found to be appropriate for sustaining large physical damages.^{53–55}

In this report, a hydrophilic and chemically reactive porous polymeric coating loaded with residual acrylate groups for systematically evaluating the impact of chemistry on designing SLIPS is introduced (Scheme 1A). Surprisingly, during the course of the study, the direct lubrication of the chemically reactive and hydrophilic interface with a range of natural and synthetic liquid lubricants allowed to develop SLIPS without associating any additional hydrophobization (Scheme 1B). However, in the past literature, hydrophobic post modification, prior to lubrication, was routinely adopted as the most essential component for designing SLIPS. In our current design of SLIPS, it was experimentally validated that the residual acrylate groups help to anchor the water immiscible lubricated phase, even though the entire porous polymeric

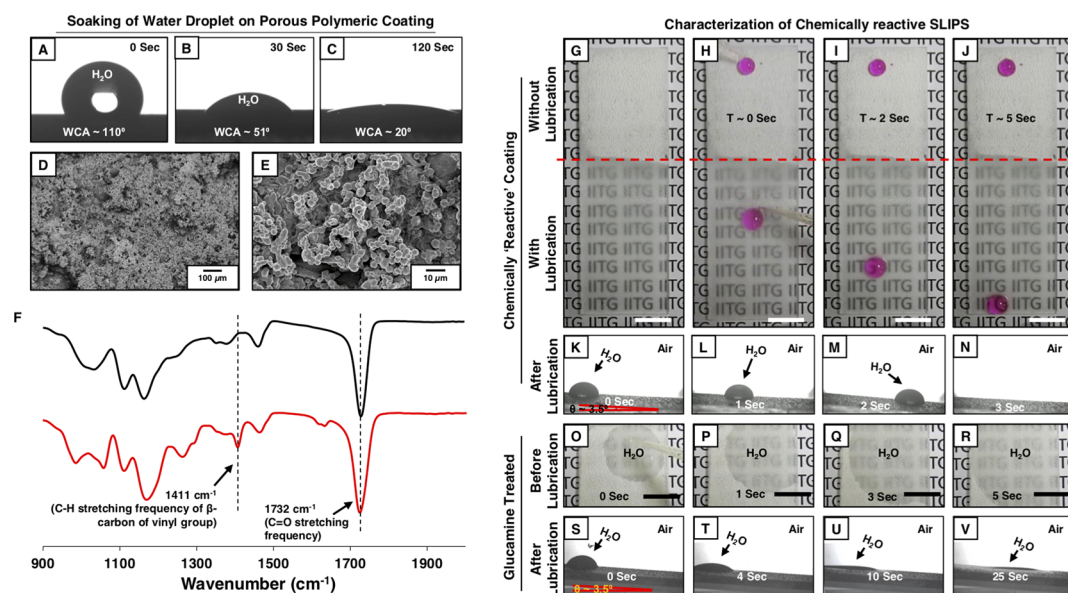


Figure 1. (A–C) Digital images illustrating wetting and spreading of a beaded water droplet ($4 \mu\text{L}$) on chemically reactive porous polymeric coating. (D–E) FESEM images of the reactive polymeric coating in low (D, scale bar: $100 \mu\text{m}$) and high (E, scale bar: $10 \mu\text{m}$) magnifications. (F) FTIR spectra of amine reactive polymeric coating before (red) and after (black) post chemical modification with glucamine. (G–J) Digital images comparing the wettability of beaded aqueous droplets on the chemically reactive polymeric coating with (bottom portion) and without (top portion) lubrication (scale bar 1 cm) with silicone oil (AR 20), where lubricated (bottom) and nonlubricated portions (top) are separated with a dotted red line. (K–N) Snapshot images illustrating the movement of beaded water droplet on the tilted (with tilting angle of 3.5°) chemically reactive SLIPS. (O–V) Digital images depicting rapid spreading and spilling of beaded water droplets on the glucamine treated polymeric coatings—both before (O–R) and after (S–V) lubrication with silicone oil.

coating remained highly hydrophilic [with a water contact angle (WCA) of $\sim 20^\circ$]. Furthermore, the readily amine reactive acrylate groups that were available in the chemically reactive porous polymeric coating allowed for systematic modulation with various alkyl amines having different hydrocarbons tail lengths, as shown in Scheme 1D,E. Moreover, various standard and severe macroscale (order of few cm) physical abrasions (e.g., sand paper abrasions, adhesive tape test, etc.) were strategically imposed on the synthesized slippery polymeric coating for exposing the interior of the polymer coating—randomly and intentionally—over a large area (in the scale of cm). However, on infusion of selected liquid lubricants, this physically damaged polymeric interface displayed Nepenthes pitcher inspired liquid wettability, as no post covalent modulation was involved in the currently synthesized SLIPS, unlike the conventional designs. Moreover, the design of chemically reactive SLIPS was successfully extended for in situ and spatially selective covalent modification with selected nucleophiles—that too using organic solvents in the presence of the lubricated phase in the porous polymeric coating.

2. RESULT

2.1. Synthesis and Characterization of Chemically Reactive SLIPS. In the past, our research group introduced a facile and catalyst free approach for synthesizing chemically reactive nanocomplexes (CRNCs) having residual acrylate groups that were readily chemically reactive towards different alkylamines through 1,4 conjugate addition reaction at ambient conditions.^{56,57} Such nanocomplexes were strategically exploited further for developing chemically reactive polymeric coatings, and the residual chemical reactivity was rationally extended for achieving extremes of liquid repellency—superhydrophobicity in air and superoleophobicity under

water.^{57–60} In this communication, the CRNC is spray deposited (see the Experimental Section for more details) for developing $245 \pm 10 \mu\text{m}$ thick polymeric coating that is inherently hydrophilic. The as synthesized polymeric coating is highly hydrophilic, where a beaded water droplet ($4 \mu\text{L}$) is gradually and continuously soaked by the polymeric coating with a WCA of 20° within 2 min, as shown in Figure 1A–C and Movie S1. The scanning electron microscopy study on the synthesized polymeric coating revealed the existence of random and covalent aggregation of nanocomplexes, as shown in Figure 1D,E and eventually, provided a porous topography and empty space for storing selected lubricants, three dimensionally.

The chemical compatibility of the lubricants with the porous matrix was an anticipated challenge before adopting nature inspired slippery property. Interestingly, the highly chemically reactive and residual acrylate moiety—in the currently synthesized porous polymeric coating, provided a simple basis to achieve essential chemical compatibility that conferred the slippery property. The existence of amine reactive acrylate groups was confirmed with Fourier transform infrared (FTIR) spectral analysis, as shown in Figure 1F. The appearance of both IR peaks at 1732 and 1411 cm^{-1} in the synthesized polymeric coating, due to vibrational stretching of carbonyl and symmetric stretching of the C–H bond of β carbon of the vinylic group, unambiguously confirmed the presence of residual acrylate groups in the hydrophilic polymeric coating.^{57–60} These residual acrylate groups also remained chemically reactive as confirmed by FTIR analysis. The normalized (with respect to IR peak at 1732 cm^{-1}) IR peak intensity at 1411 cm^{-1} significantly depleted after the mutual reaction with a primary amine containing small molecule (i.e. glucamine) through 1,4 conjugate addition reaction, where the carbonyl group remained intact and vinyl groups are

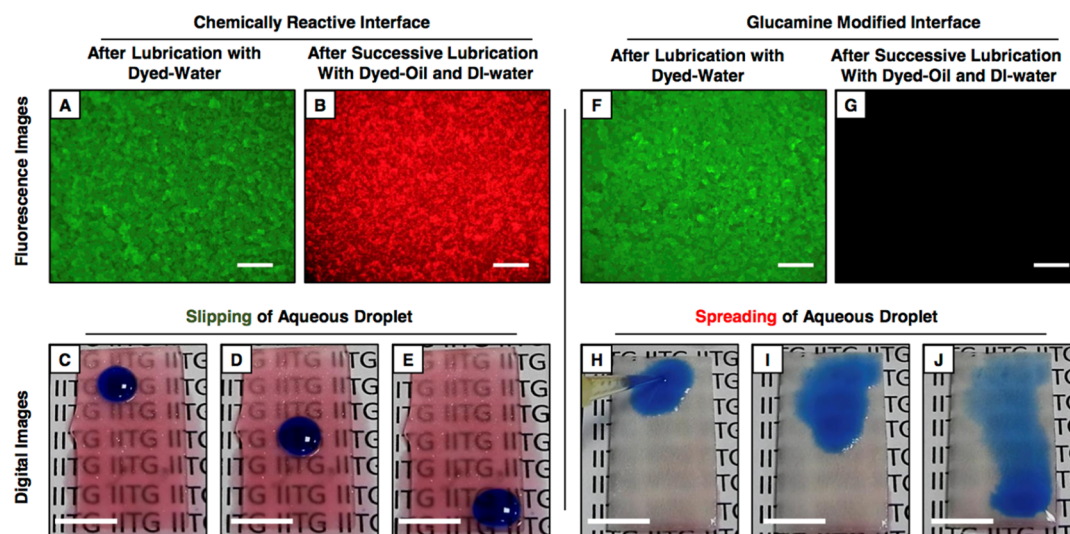


Figure 2. (A,B,F,G) Fluorescence images of the chemically reactive polymeric coating (A–B) and glucamine modified polymeric coating (F–G) after immersion in dyed (fluorescein, water soluble) aqueous phase (A, F; scale bar: $500\ \mu\text{m}$) and after successive immersion in dyed (Nile red, water immiscible) silicone oil and DI water (B,G; scale bar: $500\ \mu\text{m}$), and DI water used for washing the interface. (C–E,H–J) Digital images illustrating the wetting and spreading of beaded water droplet (scale bar 1 cm) on the tilted interface of chemically reactive (C–E) and glucamine modified (H–J) polymeric interface, which were immersed first in the aqueous phase and second in silicone oil. At the end, both the interfaces (C–E, H–J) were washed with DI water, prior to beading blue colored aqueous phase.

consumed. Thus, standard FTIR analysis revealed the existence of chemically reactive acrylate groups in the synthesized porous polymeric coating. This residual reactivity provided essential hydrophobic anchoring points for stabilizing the lubricated phase in the porous polymeric coating. Moreover, this residual chemical reactivity was extended for a systematic investigation of the impact of different chemical functionalities on bioinspired liquid infused slippery property.

Next, the chemically reactive and inherently hydrophilic porous polymeric coating was lubricated with silicone oil (AR 20), prior to examining the slipping behavior of a beaded aqueous droplet (red color aids visual inspection). The optically opaque polymeric coating instantly became translucent after lubricating with silicone oil. Then, the polymeric coating having both the dry (top opaque portion, Figure 1G) and the lubricated (translucent) region was kept with a tilting angle of 4° , prior to beading two aqueous droplets at two different portions of the coating. The aqueous droplet that beaded on the dry polymeric interface remained stationary and slowly started spreading (Figure 1H–J), whereas the aqueous droplet that beaded on the lubricated portion of the polymeric coating with a WCA of $\sim 83^\circ$, immediately slipped away from the initial position and travelled along the downslope of the inclined SLIPS, as shown in Figure 1H–J and Movie S2. Thus, the same polymeric interface that soaked the aqueous phase (Figure 1A–C) is also capable of displaying slippery property after the infusion of silicone oil. A slight change in the sliding angle and WCA was observed on increasing the dilution of spraying solution of CRNC, as shown in Table S1. In the conventional design of SLIPS, inert post modification with hydrophobic moieties were mostly adopted for achieving the chemical compatibility between the lubricated phase and polymeric coating, which is known to be an essential parameter for obtaining the slippery property. The current study experimentally validated that this additional induction of high hydrophobicity with long tail hydrocarbons or fluorinated moieties is not an essential chemical parameter to achieve SLIPS. In the synthesized SLIPS, the residual acrylate groups

are self sufficient for stabilizing the lubricant phase, and the aqueous phase readily slipped off from the tilted interface. The lubricant (silicone oil) loading capacity decreased from 7.0 ± 0.7 to $5.0 \pm 0.3\ \text{mg}/\text{cm}^2$ on lowering the thickness of the porous polymeric coating from 245 ± 10 to $150 \pm 7\ \mu\text{m}$. However, the performance of SLIPS remained unperturbed, no change in the sliding angle and water contact was noted. Further, experiments were designed to validate stabilization of the lubricant in chemically reactive SLIPS, where the chemically reactive polymeric coating loaded with residual acrylate groups was postmodified with a hydrophilic small molecule (glucamine), replacing the acrylate groups by multiple hydroxyl moieties (hydrophilic groups) of glucamine. The successful covalent modulation of the polymeric coating with glucamine was confirmed by FTIR analysis (Figure 1F). A drastic change in liquid wettability was noted for such glucamine modified polymeric coating. Aqueous droplets were instantly soaked by the glucamine treated polymeric coating with WCA of 0° , as shown in Figure 1O–R. Moreover, the lubricated phase in the glucamine treated polymeric coating became unstable on exposure to probe liquid, which resulted in the spreading of the beaded aqueous phase on lubricated polymeric coating (Figure 1S V and Figure S1). Thus, the controlled study unambiguously revealed that the residual acrylate group is instrumental for achieving the desired chemical compatibility in the synthesized chemically reactive SLIPS. Nevertheless, in the current design, any additional postcovalent modification is not required to achieve SLIPS, such demonstration is yet to be reported in the literature.

2.2. Investigation of Chemical Compatibility between the Porous Substrate and Infused Lubricants.

The synthesis of SLIPS with the hydrophilic interface, without adopting any postmodification with the hydrophobic coating is highly unusual in the literature. However, during the course of the study, it was found that the chemically reactive hydrophilic interface transformed into SLIPS after lubrication with silicone oil as discussed in the above section. This superior chemical compatibility of the as synthesized hydrophilic and chemically

reactive polymeric coatings with the lubricant phase over probe liquid (i.e., aqueous phase) was further independently revalidated with another controlled study. At first, the synthesized chemically reactive coating was submerged in the aqueous phase (added fluorescein dye aids visual inspection) for 30 s to allow infiltration of the aqueous phase, as shown in Figure S2A. This impregnation of the aqueous phase in the hydrophilic polymeric coating was confirmed by both visual inspection and fluorescence microscopy. The fluorescence signal appeared, due to the penetration of dye added aqueous phase into the porous and hydrophilic polymeric coating (Figure 2A). Next, the wet (by aqueous phase) polymeric interface was transferred into the Nile red (water immiscible dye) dyed silicone oil (model lubricant), followed by washing with deionized (DI) water for removing loosely held silicone oil (see Figure S2B and Movie S3) from top of the interface. In the end, the polymeric coating appeared to be completely red in color as the Nile red added silicone oil rapidly infiltrated into the polymeric coating, replacing the aqueous phase. Furthermore, the fluorescence microscopic study (Figure 2B) also confirmed the complete removal of the aqueous phase by the water immiscible lubricated phase in the polymeric coating. Only the fluorescence signal for Nile red dye (only soluble in the oily phase) was noted, whereas no trace of fluorescence for the water soluble dye (fluorescein) was observed from the polymeric coating (Figure 2B). As expected, the beaded aqueous phase (blue color aids visual inspection) readily slipped off from the tilted polymeric interface that was exposed to both, probe liquid (aqueous) phase, and subsequently, lubricant (silicone oil) phase (Figure 2C–E). In a separate control study, the same demonstration was repeated with glucamine treated polymeric coating, where acrylate groups were consumed through 1,4 conjugate addition reaction and hydroxyl groups were inducted in place of the acrylate groups. The outcome of the demonstration with glucamine treated polymeric coating was completely different, in comparison to the as synthesized chemically reactive and hydrophilic coatings, as shown in Movie S4. The glucamine treated polymeric coating immediately soaked the dyed aqueous phase as confirmed by both visual inspection and fluorescence microscopic images in Figure 2F and Figure S2D. However, the model lubricant phase (Nile red added silicone oil) failed to displace the infiltrated aqueous phase. As a result, no trace of fluorescence signal for Nile red dye was observed from the glucamine treated polymeric coating—even after submerging in dyed (with Nile red) silicone oil phase for 30 s (Figure 2G). This controlled study confirmed that the glucamine treated polymeric coating was chemically more compatible with the probe liquid rather than the lubricant phase. Therefore, the polymeric coating that was post modified with glucamine, completely failed to display slippery property, and the beaded water droplet completely spread on the interface, as shown in Figure 2H–J. Even though the as synthesized chemically reactive polymeric coating remained overall highly hydrophilic in air with a WCA of 20° (Figure 1C), but the affinity for the oily phase is more superior, likely due to the presence of the residual hydrophobic acrylate groups. This demonstration unambiguously and unprecedentedly revealed that the conventional post modification with long tail hydrocarbon or fluorinated molecules at the top of the SLIPS is not an essential chemical criterion for achieving the slippery property. Further, the residual acrylate groups present in the synthesized porous polymeric coating provided the essential chemical

compatibility with various other synthetic and natural lubricated phases, including vegetable oil, olive oil, and silicone oil and eventually the polymeric coating became slippery after infusion of selected lubricants, as shown in Figure S6. Moreover, various practically relevant substrates (e.g. wood, concrete, paper, aluminum foil, etc.) were successfully coated with such chemically reactive SLIPS (Figure S8). Next, different standard physical and chemical durability tests were imposed on the as synthesized SLIPS to examine its tolerance at practically relevant challenging physical settings. First, the SLIPS formed on a flexible substrate (i.e., aluminum foil) was exposed to different and relevant physical manipulations—including bending and creasing. However, the SLIPS with arbitrary creased marks continued to display uninterrupted slippery property, as shown in Figure S6C–E.

2.3. Physical and Chemical Durability of Chemically Reactive SLIPS. In the past, mostly micrometer scale scratches were introduced to mimic practically relevant harsh abrasive challenges, and the tolerance toward such minor damages was commonly examined with the previously reported SLIPS.⁵ However, the demonstration for analyzing the impact of large scale (over centimeters) physical damages, which is more relevant for practical scenarios, is few in the literature. In general, any physical abrasion over large scale is likely to remove the thin hydrophobic coating from top of the hydrophilic hierarchical interface in most of the conventional reported SLIPS, and the lack of chemical compatibility between the lubricated phase and freshly exposed hydrophilic interior in earlier reported materials was a major threat for its survival under practically more relevant and harsh physical challenges. Our current synthetic design of slippery interfaces is fundamentally different from the conventional approach. Compared to previous relevant literature, in our current design, the chemically reactive slippery interface does not require any post chemical hydrophobization on top of the featured interface. Thus, the essential chemical compatibility between chemically reactive polymeric coating and the lubricated phase should be remained intact at physically abraded interfaces. Some standard and severe abrasive tests were performed on the polymeric coating for investigating the impact of physical abrasions on the embedded slippery property. An abrasive surface of sandpaper (grid no 300) was manually rubbed on the polymeric coating 10 times, with an applied pressure of 3.27 kPa. During this abrasion process, a white powdery material piled up at the edges of the coating, and the thickness of the coating significantly reduced from 240 ± 8 to 170 ± 4 μm . However, the embedded slippery property remained intact, and a beaded water droplet (color aids visual inspection) on the physically abraded polymeric coating (kept with a tilting angle of $\sim 4^\circ$) was observed to move down the surface, as shown in Figure 3A–C. The topography of the abraded interface was further examined with field emission scanning electron microscopy (FESEM), confirming the existence of a random association of granular polymeric domains. Moreover, the sand paper abraded polymeric coating with freshly exposed interior remained loaded with residual acrylate groups as confirmed from standard FTIR analysis (see Figure S5). Thus, the abraded interface remained efficient in displaying bioinspired slippery property after lubrication with silicone oil. In another abrasion process, a freshly exposed adhesive surface was brought in contact with the polymeric coating with an applied load of 500 g. The applied external pressure secured uniform and facilitated contact between the

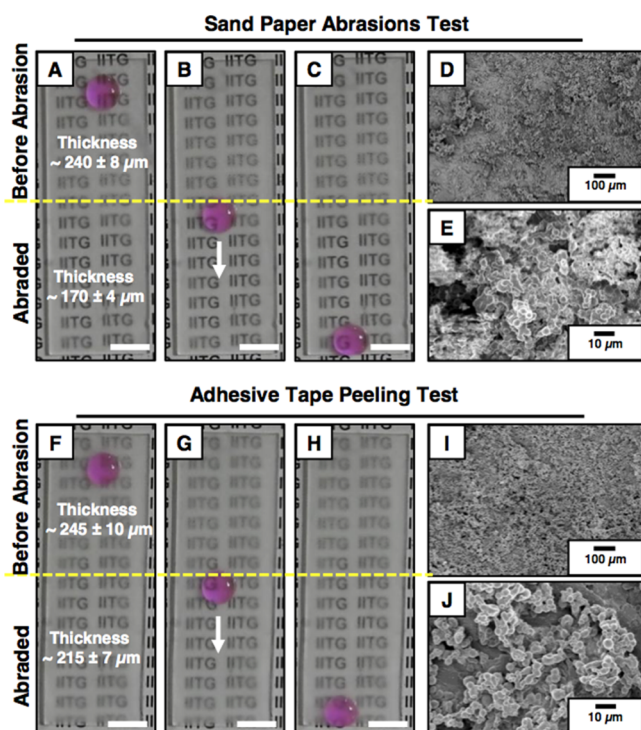


Figure 3. (A–C) Digital images comparing the slipping of beaded water droplet on both physically unaffected and sand paper abraded (denoted by bottom side of dotted yellow line) polymeric coating (tilted with 4° inclination) after being lubricated with silicone oil (AR 20) (scale bar: 1 cm). (D,E) FESEM images of the sand paper abraded polymeric coating in low (D, scale bar: $100 \mu\text{m}$) and high (E, scale bar: $10 \mu\text{m}$) magnifications. (F–H) Digital images illustrating the wettability of beaded water droplet on both the lubricated non abraded and adhesive tape abraded polymeric coating (denoted by bottom side of dotted yellow line) (scale bar: 1 cm). (I,J) FESEM images of the sand paper abraded polymeric coating in low (I, scale bar: $100 \mu\text{m}$) and high (J, scale bar: $10 \mu\text{m}$) magnifications.

adhesive surface and the top of the polymeric coating. During the process of peeling the adhesive tape from the polymeric coating, a top portion of the porous polymeric coating was fractured randomly and transferred onto the adhesive tape surface. The interior of the polymeric coating was exposed arbitrarily after this abrasion test, but the slippery property was found to be unaltered (Figure 3F–H) as the physically damaged interface still remained highly porous (see Figure 3I,J) for displaying bioinspired SLIPS. As synthesized SLIPS was found to be antifouling in different complex aqueous phases and relevant liquid food products—including highly acidic (pH 1) and alkaline (pH 13) aqueous phase, hot (85°C) coffee, cold (5°C) orange juice, and honey (see Figure 4). Further, the as synthesized polymeric coating was intentionally exposed to various other practically relevant conditions, including extremes of pH, artificial seawater, river water, and UV irradiation for the prolonged (10 days) duration before examining the liquid wettability. However, the embedded water wettability remained intact in the synthesized SLIPS, as shown in Figure S6. The infused lubricant protected the residual acrylate groups of porous polymeric coating from aqueous exposure; however, the residual acrylate groups in the chemically reactive SLIPS became readily reactive towards organic phase having amine containing small molecules.

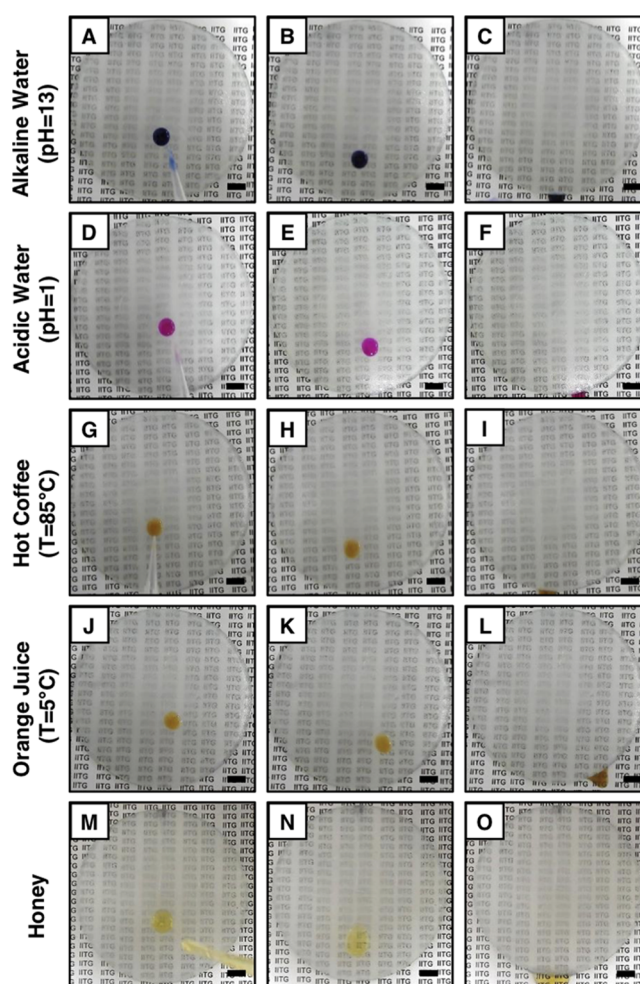


Figure 4. Digital images illustrating movement of different complex and practically relevant food products, including highly alkaline (pH 13; A–C) and acidic (pH 1; D–F) aqueous phase, hot coffee (85°C ; G–I), cold orange juice (5°C ; J–L), and honey (M–O) on silicone oil infused polymeric coating on a watch glass.

In the past, reported SLIPS remained mostly chemically inactive due to the optimization of the top of the interface with a chemically inert layer of either long tail hydrocarbon or fluorinated derivatives. On the other hand, there are few reports of chemically reactive porous interfaces, but most of them are inherently adopted with superhydrophobicity. Thus, the detailed examination of the impact of different chemical functionalities on the slippery property remained a challenge. Here, the chemically reactive and hydrophilic porous interface became SLIPS, immediately after lubrication with selected oils was further investigated for the exact role of water wettability and surface free energy for designing the liquid infused slippery interface. The residual acrylate groups allowed to adopt various functional groups through simple 1,4 conjugate addition reactions at ambient conditions, without the generation of any side products. Before lubrication with silicone oil, chemically the reactive porous polymeric coatings (having $\text{WCA} \approx 20^\circ$) were individually post modified with various alkyl amines with the gradually increasing length of the hydrocarbon tail—starting from propylamine to octadecyl amine. The successful post covalent modifications of the chemically reactive polymeric coating with different alkyl amines were characterized by FTIR analysis and calculation of

surface energy, as shown in Figure S7 and Table S2, respectively. The surface energy significantly changed depending on the selection of post covalent modifications as noted in Table S2. The polymeric coating that is treated with a lower analogue of pentylamine (i.e., propylamine and butylamine) remained extremely hydrophilic with a WCA of 0°. Unfortunately, even after lubrication, these post modified interfaces failed to display the slippery property, and beaded water droplets spread on the lubricated interface. However, the chemical postmodification of the same polymeric interface with pentylamine lead to a sharp rise in WCA from 0 to 147° in the porous polymeric coating, and the lubricated interface displayed slippery property with advancing WCA of ~86° and sliding angle of ~2°, as shown in Table 1. Further, increase in

Table 1. Accounting Water Wettability of Beaded Droplet before and after Lubrication (with Silicone Oil) of Chemically Reactive and Post Covalently Modified Polymeric Interfaces, Where Different Alkyl Amines Are Reacted Through 1,4 Conjugate Addition Reaction

coating with or without post-chemical modifications	water contact angle (°)	water wettability after infusion of silicone oil	
		θ_{CA} (°)	sliding angle (°)
reactive coating	20.3 ± 0.5	83.7 ± 0.3	2.1 ± 0.3
propylamine	0	spreading	NA
butylamine	0	spreading	NA
pentylamine	147.4 ± 0.5	85.9 ± 0.4	1.8 ± 0.6
hexylamine	148.5 ± 0.5	86.1 ± 0.3	1.8 ± 0.3
heptylamine	149.4 ± 0.6	86.2 ± 0.4	1.8 ± 0.2
octylamine	151.7 ± 0.4	86.3 ± 0.4	1.8 ± 0.7
decylamine	154.3 ± 0.4	87.5 ± 0.4	1.8 ± 0.4
dodecylamine	154.1 ± 0.7	87.5 ± 0.6	1.7 ± 0.4
octadecylamine	155.7 ± 0.7	87.7 ± 0.5	1.6 ± 0.5

the hydrocarbon chain length of the selected alkyl amines for post chemical modification of the chemically reactive porous coating provided porous polymeric coating with higher WCA; however, this increase in WCA has merely any impact on

lubricated interfaces, as shown in Table 1, where the slip angle and WCAs remain very similar for all polymeric coatings that were treated with higher analogues than pentylamine. Thus, the tailoring of the interface with molecules having a long hydrocarbon tail above the pentyl moiety is not necessary for the synthesis of SLIPS, even the modification of the porous interface with molecules having shorter hydrocarbon is capable of displaying the slippery property. To examine the performance of SLIPS with different alkylamine modifications, the SLIPS was submerged in the aqueous phase multiple times (5000 times), and after regular intervals, both WCA and WSA were recorded. With increasing the number of dipping of differently post modified SLIPS in water, the WSA on all SLIPS increased gradually; however the increment is more with decreasing the hydrocarbon tail length in the post modified SLIPS, as shown in Figure S8.

2.4. In Situ and Spatially Selective Covalent Modification of the Chemically Reactive SLIPS. In general, an aqueous ink was used for spatially selective and contact based post covalent modification to achieve the patterned interface with specific functional groups that display hydrophilicity/slippy wettability. However, a report of the spatially selective modification directly using organic solvents is yet to be reported as the organic liquids with low surface tension can arbitrarily spill and spread on commonly used solid and dry interface in air. Accordingly, spatially selective deposition of any water insoluble functional molecules (i.e. conductive polymer, catalyst, etc.) is a persistent challenge. In general, the conventional SLIPS is chemically inert as the post modification with long tail hydrocarbons or fluorinated molecules are mandatorily associated, prior to the lubrication process. The currently synthesized chemically reactive porous polymeric coating that act as a base layer to infuse a selected lubricant is capable of reacting with primary amine containing small molecules through 1,4 conjugate addition reaction in the organic medium following two independent processes. The covalent modification that was performed before lubrication of the chemically reactive base layer is referred as premodified SLIPS, and the modification of the lubricated polymeric

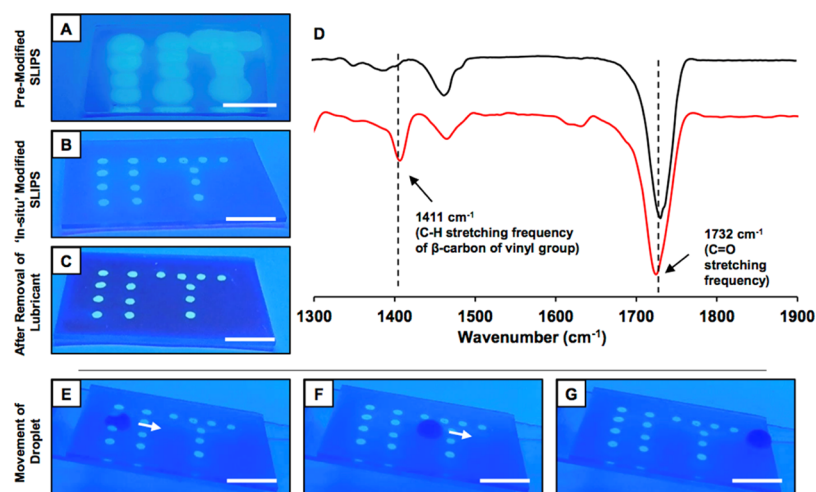


Figure 5. (A,B) Digital images of chemically reactive SLIPS that are premodified (A, modification before lubrication) and in situ modified (B, modification directly on lubricated surface) with solution of dansyl cadaverine (DC) in methanol. (C) Digital image of in situ modified SLIPS after the removal of lubricate phase. (D) FTIR spectra of chemically reactive SLIPS with (black) and without (red) in situ chemical modification through 1,4 conjugate addition reaction with DC. (E-G) Digital images illustrating the translation of beaded aqueous droplet on in situ modified SLIPS. All the digital images are acquired under UV light. Scale bars are 1 cm.

coating is denoted as “in situ” modified SLIPS. In this current study, the synthesized chemically reactive SLIPS was unprecedentedly extended for spatially selective and “in situ” covalent modification with a primary amine containing nucleophile, even in the presence of the lubricated phase in the porous polymeric coating. The lubricant infused chemically reactive interface was directly and spatially selectively exposed to solutions of selected nucleophiles in an organic solvent having low surface tension. In the current study, two different approaches—(a) premodification and (b) in situ modification of chemically reactive SLIPS were adopted for direct comparison of its ability in developing spatially selective postcovalent modification. The pattern in the form of “IIT” was generated on a chemically reactive SLIPS by transferring a series of droplets (0.7 μL) of dansyl cadaverine (DC) solution in methanol (MeOH) at different locations of polymeric coating before (denoted as pre modification) and after (referred as in situ modification) lubrication. Prior to the lubrication of the polymeric coating, the solution of DC in MeOH randomly and immediately spread on the dry polymeric coating, as revealed under UV light (Figure 5A). However, the polymeric coating remained slippery after the infusion of the lubricant, as shown in Figure S9. In comparison, after lubrication, a chemically reactive SLIPS was exposed to a solution of DC in MeOH to prepare a spatially selective postmodification through 1,4 conjugated addition reaction at ambient condition. In the end, a pattern of “IIT” was generated with well defined circular spots under UV light (Figure 5B). Moreover, this pattern remained stable even after removal of the lubricant phase from the polymeric coating, as shown in Figure 5C. This simple study confirmed the successful transfer of DC to the polymeric coating through the lubricant phase, without any arbitrary spillage. Further, the exposure of DC solution to chemically reactive SLIPS caused a significant depletion of the IR peak at 1411 cm^{-1} in the polymeric coating, which revealed the in situ 1,4 conjugate addition reaction between amine of DC and residual acrylate groups of the SLIPS at ambient condition (Figure 5D). Even after the in situ modification of the SLIPS with the selected nucleophile, the slippery property remained intact, as shown in Figure 5E–G. Thus, the current design provided a simple basis for well defined and spatially selective in situ modification of the chemically reactive SLIPS with primary amine containing nucleophiles. This principle can be used for developing multifunctional SLIPS.

3. CONCLUSIONS

In summary, a chemically reactive SLIPS was rationally introduced through strategic association of residual acrylate groups in the inherently hydrophilic porous polymeric spray coating, where acrylate groups not only allow the adaptation of chemical reactivity through simple 1,4 conjugate addition reaction at ambient condition but also provide essential chemical compatibility towards various selected lubricants, without requiring any hydrophobization. Eventually, after selected lubrication, the hydrophilic polymeric coating loaded with chemically reactive residual functionality displayed slippery property. The as synthesized chemically reactive SLIPS are highly tolerant towards various physical and chemical challenges. The impact of different chemical modulation was investigated in details through post covalent modification of the residual acrylate groups with selected alkyl amines. Further, various nucleophiles could be strategically and

covalently embedded following an in situ modification process for developing different functional SLIPS.

4. EXPERIMENTAL SECTION

4.1. Materials. Branched polyethelenimine (BPEI, MW $\approx 25\,000$ Da) and dipentaerythritol penta /hexa acrylate (5 Acl, MW $\approx 524.21\text{ g mol}^{-1}$) were purchased from sigma Aldrich. Silicon oil (AR 20), octadecylamine (97%), dodecylamine (98%), decylamine (95%), octylamine (99%), heptylamine (99%), hexylamine (99%), pentyl amine (95%), and propylamine (98%) were bought from Sigma Aldrich. Butylamine (98%) was purchased from Spectrochem. Glucamine (95%) and Nile red were procured from TCI chemicals, India. Fluorescein was obtained from Loba Chemie. Pentanol was obtained from Alfa Aesar. Microscope slides acquired from Zenith India. Spray bottle (capacity $\approx 100\text{ mL}$, nozzle diameter $\approx 400\ \mu\text{m}$) was purchased from Amazon India. Adhesive tape, paper, aluminium foil, and sandpaper (300 grit) were procured from a local stationary shop. Concrete and wooden block were collected from a local construction site. Glass slides were thoroughly washed using ethanol prior to experiments.

4.2. Characterization. All FTIR spectra were obtained using standard KBr plate by PerkinElmer instruments. All FESEM images were acquired using a Carl Zeiss scanning electron microscope (prior to experiment each sample were coated with a thin layer of conducting gold). The microscopic images were obtained by a OLYMPUS BX51 microscope. All contact angles measured using a Drop shape Analyser DSA25 at $25\text{ }^\circ\text{C}$. The advancing/receding were taken with Milli Q water droplet, respectively, at four different regions of each surface. The surface free energy was calculated using a Drop Shape Analyser DSA25 at $25\text{ }^\circ\text{C}$, where water and hexane are polar and dispersive phase, respectively. Digital photographs were taken using a Nikon COOLPIX, B700 point shot camera. The thickness of the coating measured by a Veeco Dektak 150 surface profilometer.

4.3. Fabrication of Reactive Polymeric Coating. The “reactive” porous polymeric coatings were prepared by spray deposition of CRNC onto the glass substrates, using a commercially available spray bottle. The reactive nanocomplexes (RNC) were prepared first by mixing two mutually reactive reactants, which are 10 mL of 5 Acl (0.1325 g/mL) and 3 mL of BPEI (0.05 g/mL) in pentanol, where the reaction medium was kept under vigorous agitation for 5 min. Then, a turbid reaction mixture (13 mL) was manually sprayed onto selected substrates over an area of 200 cm^2 from a distance of 15 cm using a commercially available spraying bottle. After deposition of CRNC, the substrates were kept in open air for the evaporation of the reaction medium.

4.4. Post Chemical Modification. The “reactive” polymeric coatings were further postmodified with primary amine containing small molecules, for example, octadecylamine (2.5 mg/mL), dodecyl amine (5 mg/mL), decylamine (0.1 mL/mL), octylamine (0.1 mL/mL), heptylamine (0.1 mL/mL), hexylamine (0.1 mL/mL), pentyl amine (0.1 mL/mL), and glucamine (2.5 mg/mL) through 1,4 conjugate addition reaction at ambient condition. After post modification, the postfunctionalized substrates were thoroughly washed with ethanol/water and kept in open air for drying.

4.5. Infusion of Selected Lubricants into Chemically Reactive and Postmodified Porous Polymeric Coating. The porous polymeric coatings ($7.5\text{ cm} \times 2.5\text{ cm}$) were infused with different lubricants (silicone oil, soybean oil, olive oil, etc.). In brief, 200 μL of lubricant spread to a porous matrix using a weighing paper over an area of 18.75 cm^2 , and the excess oil was removed by vertically placing the substrates for 15 min.

4.6. Physical and Chemical Durability of the Reactive SLIPS. All the physical/chemical robustness descriptions performed using reactive porous polymeric coating. An adhesive tape test was carried out by placing an adhesive surface ($3\text{ cm} \times 2.5\text{ cm}$) onto the polymeric coating with a weight of 500 g, and after 5 min, the tape was taken out randomly. Some visual damages were found to have occurred on the coating but the sliding behavior of water droplets remains unperturbed after the infusion of silicone oil. Sand paper

abrasion was performed by placing a sand paper (grit no 300, 3 cm × 2 cm) which was fixed on glass slide, on half of the polymeric coating using an external pressure and rubbed the surface back and forth 10 times. Random damages occurred as some portion of the reactive coating came out with the sand paper and water sliding behavior examined by contact angle measurements and digital photograph after the infusion of silicone oil. For the chemical durability test, silicone oil infused polymeric surfaces (glass as model substrate) were submerged in different aqueous environments, for example, acidic water (pH = 1), alkaline water (pH = 13), river water, and artificial sea water for 10 days. The liquid water wettability examined by contact angle measurements for each substrate. Further, the porous polymeric coatings on a glass substrate were kept continuously under UV irradiation for 10 days, and on every 5 days of interval, the water wettability was examined by contact angle measurements.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.9b22469>.

Impact of selected chemical modification on the slippery property, successful post covalent modification with various alkyl amines, the ability for antifouling various complex aqueous phases, physical and chemical durability, coating on various relevant objects, and impact of spatially selective premodification using an organic solvent (PDF)

Beaded water droplet (4 μL) gradually and continuously soaked into the polymeric coating with a WCA of 20° within 2 min (AVI)

Aqueous droplet beaded on the lubricated portion of the polymeric coating with a WCA of ~83 (AVI)

Wet (by aqueous phase) polymeric interface transferred into the Nile red (water immiscible dye) dyed silicone oil (model lubricant) (AVI)

Glucamine treated polymeric coating immediately soaked with a dyed aqueous phase (AVI)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the financial support from the Board of Research in Nuclear Sciences (BRNS) (34/20/31/2016 BRNS, DAE YSRA). We thank CIF, Centre for Nano

technology and Department of Chemistry, Indian Institute of Technology, Guwahati, for their generous assistance in executing various experiments and for the infrastructure. We acknowledge the support from Ministry of Electronics and Information Technology (grant no. 5(9)/2012 NANO). K.M. is thankful to IIT, Guwahati, for his doctoral fellowships. M.H. and U.M. acknowledge support by the DAAD in the form of an academic exchange fellowship (program Bilateral Exchange of Academics).

■ REFERENCES

- (1) Li, X. M.; Reinhoudt, D.; Crego Calama, M. What do We Need for a Superhydrophobic Surface? A Review on the Recent Progress in the Preparation of Superhydrophobic Surfaces. *Chem. Soc. Rev.* **2007**, *36*, 1350–1368.
- (2) Chu, Z.; Feng, Y.; Seeger, S. Oil/water Separation with Selective Superwetting/Superwetting Surface Materials. *Angew. Chem., Int. Ed.* **2015**, *54*, 2328–2338.
- (3) Su, B.; Tian, Y.; Jiang, L. Bioinspired Interfaces with Superwettability: From Materials to Chemistry. *J. Am. Chem. Soc.* **2016**, *138*, 1727–1748.
- (4) Lai, Y.; Huang, Z.; Ge, M.; Zhang, K. Q.; Chen, Z.; Chi, L.; Chi. Recent Advances in TiO₂ Based Nanostructured Surfaces with Controllable Wettability and Adhesion. *Small* **2016**, *12*, 2203–2224.
- (5) Wong, T. S.; Kang, S. H.; Tang, S. K. Y.; Smythe, E. J.; Hatton, B. D.; Grinthal, A.; Aizenberg, J. Bioinspired Self Repairing Slippery Surfaces with Pressure Stable Omnipobicity. *Nature* **2011**, *477*, 443–447.
- (6) Anand, S.; Paxson, A. T.; Dhiman, R.; Smith, J. D.; Varanasi, K. K. Enhanced Condensation on Lubricant Impregnated Nanotextured Surfaces. *ACS Nano* **2012**, *6*, 10122–10129.
- (7) Kim, P.; Wong, T. S.; Alvarenga, J.; Kreder, M. J.; Adorno Martinez, W. E.; Aizenberg, J. Liquid Infused Nanostructured Surfaces with Extreme Anti Ice and Anti Frost Performance. *ACS Nano* **2012**, *6*, 6569–6577.
- (8) Yao, X.; Hu, Y.; Grinthal, A.; Wong, T. S.; Mahadevan, L.; Aizenberg, J. Adaptive Fluid Infused Porous Films with Tunable Transparency and Wettability. *Nat. Mater.* **2013**, *12*, 529–534.
- (9) Subramanyam, S. B.; Azimi, G.; Varanasi, K. K. Designing Lubricant Impregnated Textured Surfaces to Resist Scale Formation. *Adv. Mater. Interfaces* **2014**, *1*, 1300068.
- (10) Manabe, K.; Kyung, K. H.; Shiratori, S. Biocompatible Slippery Fluid Infused Films Composed of Chitosan and Alginate via Layer by Layer Self Assembly and Their Antithrombogenicity. *ACS Appl. Mater. Interfaces* **2015**, *7*, 4763–4771.
- (11) Wang, Y.; Zhang, H.; Liu, X.; Zhou, Z. Slippery Liquid Infused Substrates: A Versatile Preparation, Unique Anti Wetting and Drag Reduction Effect on Water. *J. Mater. Chem. A* **2016**, *4*, 2524–2529.
- (12) Guo, J.; Fang, W.; Welle, A.; Feng, W.; Filpponen, I.; Rojas, O. J.; Levkin, P. A. Superhydrophobic and Slippery Lubricant Infused Flexible Transparent Nanocellulose Films by Photoinduced Thiol–Ene Functionalization. *ACS Appl. Mater. Interfaces* **2016**, *8*, 34115–34122.
- (13) Park, K. C.; Kim, P.; Grinthal, A.; He, N.; Fox, D.; Weaver, J. C.; Aizenberg, J. Condensation on Slippery Asymmetric Bumps. *Nature* **2016**, *531*, 78–82.
- (14) Yu, L.; Chen, G. Y.; Xu, H.; Liu, X. Substrate Independent, Transparent Oil Repellent Coatings with Self Healing and Persistent Easy Sliding Oil Repellency. *ACS Nano* **2016**, *10*, 1076–1085.
- (15) Wu, Y.; Zhou, S.; You, B.; Wu, L. Bioinspired Design of Three Dimensional Ordered Tribachia Post Arrays with Reentrant Geometry for Omnipobic and Slippery Surfaces. *ACS Nano* **2017**, *11*, 8265–8272.
- (16) Dai, X.; Sun, N.; Nielsen, S. O.; Stogin, B. B.; Wang, J.; Yang, S.; Wong, T. S. Hydrophilic Directional Slippery Rough Surfaces for Water Harvesting. *Sci. Adv.* **2018**, *4*, No. eaaq0919.

- (17) McBride, S. A.; Dash, S.; Varanasi, K. K. Evaporative Crystallization in Drops on Superhydrophobic and Liquid Impregnated Surfaces. *Langmuir* **2018**, *34*, 12350–12358.
- (18) Park, K. C.; Kim, P.; Grinthal, A.; He, N.; Fox, D.; Weaver, J. C.; Aizenberg, J. Condensation on Slippery Asymmetric Bumps. *Nature* **2016**, *531*, 78–82.
- (19) Howell, C.; Grinthal, A.; Sunny, S.; Aizenberg, M.; Aizenberg, J. Designing Liquid Infused Surfaces for Medical Applications: A Review. *Adv. Mater.* **2018**, *30*, 1802724.
- (20) Kreder, M. J.; Alvarenga, J.; Kim, P.; Aizenberg, J. Design of Anti Icing Surfaces: Smooth, Textured or Slippery? *Nat. Rev. Mater.* **2016**, *1*, 15003.
- (21) Wang, W.; Timonen, J. V. I.; Carlson, A.; Drotlef, D. M.; Zhang, C. T.; Kolle, S.; Grinthal, A.; Wong, T. S.; Hatton, B.; Kang, S. H.; Kennedy, S.; Chi, J.; Blough, R. T.; Sitti, M.; Mahadevan, L.; Aizenberg, J. Multifunctional ferrofluid infused surfaces with reconfigurable multiscale topography. *Nature* **2018**, *559*, 77–82.
- (22) Hou, X.; Li, J.; Tesler, A.; Yao, Y.; Wang, M.; Min, L.; Sheng, Z.; Aizenberg, J. Dynamic Air/Liquid Pockets for Guiding Microscale Flow. *Nat. Commun.* **2018**, *9*, 733.
- (23) Rapoport, L.; Solomon, B. R.; Varanasi, K. K. Mobility of Yield Stress Fluids on Lubricant Impregnated Surfaces. *ACS Appl. Mater. Interfaces* **2019**, *11*, 16123–16129.
- (24) Manabe, K.; Matsubayashi, T.; Tenjimbayashi, M.; Moriya, T.; Tsuge, Y.; Kyung, K. H.; Shiratori, S. Controllable Broadband Optical Transparency and Wettability Switching of Temperature Activated Solid/Liquid Infused Nanofibrous Membranes. *ACS Nano* **2016**, *10*, 9387–9396.
- (25) Chen, X. c.; Ren, K. f.; Wang, J.; Lei, W. x.; Ji, J. Infusing Lubricant onto Erasable Microstructured Surfaces toward Guided Sliding of Liquid Droplets. *ACS Appl. Mater. Interfaces* **2017**, *9*, 1959–1967.
- (26) Scarratt, L. R. J.; Zhu, L.; Neto, C. How Slippery are SLIPS? Measuring Effective Slip on Lubricated Surfaces with Colloidal Probe Atmoc Force Microscopy. *Langmuir* **2019**, *35*, 2976–2982.
- (27) Xiang, T.; Zhang, M.; Sadig, H. R.; Li, Z.; Zhang, M.; Dong, C.; Yang, L.; Chan, W.; Li, C. Slippery Liquid Infused Porous Surface for Corrosion Protection with Self Healing Property. *Chem. Eng. J.* **2018**, *345*, 147–155.
- (28) Kratochvil, M. J.; Welsh, M. A.; Manna, U.; Ortiz, B. J.; Blackwell, H. E.; Lynn, D. M. Slippery Liquid Infused Porous Surfaces that Prevent Bacterial Surface Fouling and Inhibit Virulence Phenotypes in Surrounding Planktonic Cells. *ACS Infect. Dis.* **2016**, *2*, 509–517.
- (29) Tenjimbayashi, M.; Togasawa, R.; Manabe, K.; Matsubayashi, T.; Moriya, T.; Komine, M.; Shiratori, S. Liquid Infused Smooth Coating with Transparency, Super Durability, and Extraordinary Hydrophobicity. *Adv. Funct. Mater.* **2016**, *26*, 6693–6702.
- (30) He, W.; Liu, P.; Jiang, J.; Liu, M.; Li, H.; Zhang, J.; Luo, Y.; Cheung, H. Y.; Yao, X. Development of Multifunctional Liquid Infused Materials by Printing Assisted Functionalization on Porous Nanocomposites. *J. Mater. Chem. A* **2018**, *6*, 4199–4208.
- (31) Wang, J.; Gao, W.; Zhang, H.; Zou, M.; Chen, Y.; Zhao, Y. Programmable Wettability on Photocontrolled Graphene Film. *Sci. Adv.* **2018**, *4*, No. eaat7392.
- (32) Guo, P.; Wang, Z.; Heng, L.; Zhang, Y.; Wang, X.; Jiang, L. Magnetocontrollable Droplet and Bubble Manipulation on a Stable Amphibious Slippery Gel Surface. *Adv. Funct. Mater.* **2019**, *29*, 1808717.
- (33) Paulssen, D.; Hardt, S.; Levkin, P. A. Droplet Sorting and Manipulation on Patterned Two Phase Slippery Lubricant Infused Surface. *ACS Appl. Mater. Interfaces* **2019**, *11*, 16130–16138.
- (34) Huang, Y.; Stogin, B. B.; Sun, N.; Wang, J.; Yang, S.; Wong, T. S. A Switchable Cross Species Liquid Repellent Surface. *Adv. Mater.* **2017**, *29*, 1604641.
- (35) Wang, Z.; Liu, Y.; Guo, P.; Heng, L.; Jiang, L. Photoelectric Synergetic Responsive Slippery Surfaces Based on Tailored Anisotropic Films Generated by Interfacial Directional Freezing. *Adv. Funct. Mater.* **2018**, *28*, 1801310.
- (36) Manabe, K.; Matsubayashi, T.; Tenjimbayashi, M.; Moriya, T.; Tsuge, Y.; Kyung, K. H.; Shiratori, S. Controllable Broadband Optical Transparency and Wettability Switching of Temperature Activated Solid/Liquid Infused Nanofibrous Membranes. *ACS Nano* **2016**, *10*, 9387–9396.
- (37) Zhan, K.; Hou, X.; Microscale, T. Tunable Microscale Porous Systems with Dynamic Liquid Interfaces. *Small* **2018**, *14*, 1703283.
- (38) Bazyar, H.; Lv, P.; Wood, J. A.; Porada, S.; Lohse, D.; Lammertink, R. G. H. Liquid–Liquid Displacement in Slippery Liquid Infused Membranes (SLIMs). *Soft Matter* **2018**, *14*, 1780–1788.
- (39) Hou, X. Liquid Gating Membrane. *Natl. Sci. Rev.* **2020**, *7*, 9.
- (40) Liu, W.; Wang, M.; Sheng, Z.; Zhang, Y.; Wang, S.; Qiao, L.; Hou, Y.; Zhang, M.; Hou, X. Mobile Liquid Gating Membrane System for Smart Piston and Valve Applications. *Ind. Eng. Chem. Res.* **2019**, *58*, 11976–11984.
- (41) Chen, Z.; Wang, H.; Tang, Y.; Wang, M.; Huang, L.; Min, L.; Meng, H.; Chen, S.; Jiang, L.; Hou, X. Liquid Gating Elastomeric Porous System with Dynamically Controllable Gas/Liquid Transport. *Sci. Sci. Adv.* **2018**, *4*, No. eaao6724.
- (42) Bazyar, H.; Javadpour, S.; Lammertink, R. G.H. On the Gating Mechanism of Slippery Liquid Infused Porous Membranes. *Adv. Mater. Interfaces* **2016**, *3*, 1600025.
- (43) Hou, X. Smart Gating Multi Scale Pore/Channel Based Membranes. *Adv. Mater.* **2016**, *28*, 7049–7064.
- (44) Buck, M. E.; Schwartz, S. C.; Lynn, D. M. Superhydrophobic Thin Films Fabricated by Reactive Layer by Layer Assembly of Azlactone Functionalized Polymers. *Chem. Mater.* **2010**, *22*, 6319–6327.
- (45) Manna, U.; Broderick, A. H.; Lynn, D. M. Chemical Patterning and Physical Refinement of Reactive Superhydrophobic Surfaces. *Adv. Mater.* **2012**, *24*, 4291–4295.
- (46) Li, J.; Li, L.; Du, X.; Feng, W.; Welle, A.; Trapp, O.; Grunze, M.; Hirtz, M.; Levkin, P. A. Reactive Superhydrophobic Surface and Its Photoinduced Disulfide ene and Thiol ene (Bio)functionalization. *Nano Lett.* **2015**, *15*, 675–681.
- (47) Kreder, M. J.; Alvarenga, M. J.; Kim, J.; Aizenberg, J. Design of Anti Icing Surfaces: Smooth, Textured or Slippery? *Nat. Rev. Mater.* **2016**, *1*, 15003.
- (48) Kim, P.; Kreder, M. J.; Alvarenga, J.; Aizenberg, J. Hierarchical or Not? Effect of the Length Scale and Hierarchy of the Surface Roughness on Omniphobicity of Lubricant Infused Substrates. *Nano Lett.* **2013**, *13*, 1793–1799.
- (49) You, I.; Lee, T. G.; Nam, Y. S.; Lee, H. Fabrication of a Micro omniphilic Device by Omniphilic/Omniphobic Patterning on Nanostructured Surfaces. *ACS Nano* **2014**, *8*, 9016–9024.
- (50) Vogel, N.; Belisle, R. A.; Hatton, B.; Wong, T. S.; Aizenberg, J. Transparency and Damage Tolerance of Patternable Omniphobic Lubricated Surfaces Based on Inverse Colloidal Monolayers. *Nat. Commun.* **2013**, *4*, 2176.
- (51) Manna, U.; Lynn, D. M. Fabrication of Liquid Infused Surfaces Using Reactive Polymer Multilayers: Principles for Manipulating the Behaviors and Mobilities of Aqueous Fluids on Slippery Liquid Interfaces. *Adv. Mater.* **2015**, *27*, 3007–3012.
- (52) Huang, W. P.; Chen, X.; Hu, M.; Hu, D. F.; Wang, J.; Li, H. Y.; Ren, K. F.; Ji, J. Patterned Slippery Surface through Dynamically Controlling Surface Structures for Droplet Microarray. *Chem. Mater.* **2019**, *31*, 834–841.
- (53) Wei, Q.; Schlaich, C.; Prévost, S.; Schulz, A.; Böttcher, C.; Gradzielski, M.; Qi, Z.; Haag, R.; Schalley, C. A. Supramolecular Polymers as Surface Coatings: Rapid Fabrication of Healable Superhydrophobic and Slippery Surfaces. *Adv. Mater.* **2014**, *26*, 7358–7364.
- (54) Liu, M.; Wang, Z.; Liu, P.; Wang, Z.; Yao, H.; Yao, X. Supramolecular Silicone Coating Capable of Strong Substrate Bonding, Readily Damage Healing, and Easy Oil Sliding. *Sci. Adv.* **2019**, *5*, No. eaaw5643.
- (55) Zhou, J.; Han, P.; Liu, M.; Zhou, H.; Zhang, Y.; Jiang, J.; Liu, P.; Wei, Y.; Song, Y.; Yao, X. Self Healable Organogel Nanocomposite

with Angle Independent Structural Colors. *Angew. Chem., Int. Ed.* **2017**, *56*, 10462–10466.

(56) Bechler, S. L.; Lynn, D. M. Reactive Polymer Multilayers Fabricated by Covalent Layer by Layer Assembly: 1,4 Conjugate Addition Based Approaches to the Design of Functional Biointerfaces. *Biomacromolecules* **2012**, *13*, 1523–1532.

(57) Rather, A. M.; Manna, U. Facile Synthesis of Tunable and Durable Bulk Superhydrophobic Material from Amine “Reactive” Polymeric Gel. *Chem. Mater.* **2016**, *28*, 8689–8699.

(58) Parbat, D.; Manna, U. Synthesis of ‘Reactive’ and Covalent Polymeric Multilayer Coatings With Durable Superoleophobic and Superoleophilic Properties Under Water. *Chem. Sci.* **2017**, *8*, 6092–6102.

(59) Rather, A. M.; Mahato, S.; Maji, K.; Gogoi, N.; Manna, U. ‘Reactive’ Nano Complex Coated Medical Cotton: A Facile Avenue for Tailored Release of Small Molecules. *Nanoscale* **2017**, *9*, 16154–16165.

(60) Maji, K.; Manna, U. Hierarchically Featured and Substrate Independent Bulk Deposition of ‘Reactive’ Polymeric Nanocomplexes for Controlled and Strategic Manipulation of Durable Biomimicking Wettability. *J. Mater. Chem. A* **2018**, *6*, 6642–6653.