

Facile Chemical Approaches to Derive Scalable and Tolerant Liquid Repellent Surfaces

A thesis submitted by

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In Partial Fulfilment of the Requirements

for the Degree of
Doctor of Philosophy



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16th January 2024



Dedicated to my parents



Indian Institute of Technology Guwahati
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STATEMENT

I hereby declare that the work incorporated in this thesis entitled “**Facile Chemical Approaches to Derive Scalable and Tolerant Liquid Repellent Surfaces**” is the result of investigations of research work carried out by me in the Department of Chemistry, under the supervision of Dr. Uttam Manna, Associate Professor, Department of Chemistry, Indian Institute of Technology Guwahati, Assam, India.

Research materials used in this thesis from any other sources have been fully cited and acknowledged. This work is original and has not been submitted elsewhere for the award of any degree.

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CERTIFICATE

This is to certify that the work presented in this thesis entitled “**Facile Chemical Approaches to Derive Scalable and Tolerant Liquid Repellent Surfaces**” by Manideepa Dhar, a PhD student of the Department of Chemistry, Indian Institute of Technology Guwahati, for the award of the degree of Doctor of Philosophy has been carried out under my supervision and this work has not been submitted elsewhere for the award of any degree.

16th January 2024

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Manideepa Dhar

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Abbreviation

SH	Superhydrophobic
CAH	Contact angle hysteresis
PTFE	Polytetrafluoroethylene
COF	Covalent organic framework
SHS	Superhydrophobic Surface
SLIPS	Slippery liquid-infused porous surfaces
MS	Microstructured
MNS	Micro/nanostructured
TO	Titanium oxide
RH	Relative humidity
Al	Aluminium
SiO ₂	Silicon dioxide
Mg	Magnesium
NaCl	Sodium Chloride
TiO ₂	Titanium dioxide
NaOH	Sodium hydroxide
H ₂ SO ₄	Sulphuric acid
UV	Ultraviolet
PDMS	poly(dimethylsiloxane)
CNF	Cellulose nanofiber
AFM	Atomic force microscopy
PAA	Poly(acrylic acid)
AEAPTMS	3-(2-aminoethylamino)propyltrimethoxysilane
ODAc	Octadecyl acrylate
HAc	Hexyl acrylate
DDAc	Dodecyl acrylate
SDS	Sodium dodecyl sulphate
CTAB	Cetyltrimethylammonium bromide
DCM	Dichloromethane
MF	Melamine formaldehyde
NaCl	Sodium chloride

MgCl ₂	Magnesium chloride
MgSO ₄	Magnesium sulphate
CaCl ₂	Calcium chloride
FESEM	Field Emission Scanning electron microscope
FTIR-ATR	Fourier transform infrared attenuated total reflectance spectra
CRPNC	Chemically reactive and polymeric nanocomplex
DS	Deposition solution
CA	Contact angle
WCA	Water contact angle
HAc	Hexyl acrylate
DDAc	Dodecyl acrylate
3-AcI	Pentaerythritol triacrylate
5-AcI	Dipentaerythritol penta-acrylate
RM	Reaction mixture
RMT	Reaction mixture type
DTAB	(1-dodecyl)trimethylammonium bromide
EDX	Energy dispersive X-ray
BPEI	Branched poly(ethyleneimine)
HA	2-hydroxy acrylate
ODA	Octadecyl amine
THF	Tetrahydrofuran
DLS	Dynamic light scattering
Glu	Glutaraldehyde
CNN	Convolution neural network
Conv2D	2-dimensional convolution layers
ReLU	Rectified linear unit
QR	Quick response
MOF	Metal–organic framework
DMF	Dimethyl formamide
DIM	Diiodomethane
DMSO	Dimethyl sulphoxide
DSC	Differential scanning calorimetry

PODAc	Poly octadecyl acrylate
PLAc	Poly lauryl acrylate
PHAc	Poly hexyl acrylate
SA	Sliding angle
XRD	X-ray diffraction
NMR	Nuclear Magnetic Resonance



Abstract

Nature inspired liquid-repellent surfaces, such as superhydrophobic and slippery surfaces, have gained enormous attention because of their potential applications in environmental remediation, anti-corrosion, self-cleaning, biomedical devices and so on. In the past, several approaches were adopted to develop artificial surfaces with desired wettability. However, significant challenges, such as poor durability and mechanical and chemical robustness, continue to impede its real-world application. This synopsis report outlines the strategic utilization of a facile and catalyst-free 1, 4-conjugate addition reaction between amine and acrylate functional groups for developing liquid-repellent surfaces with enhanced robustness following a simple, scalable, and rapid fabrication approach. The synopsis report entitled “*Facile Chemical Approaches to Derive Scalable and Tolerant Liquid Repellent Surfaces*” is divided into six chapters. **Chapter 1** gives a concise overview of bio-inspired wettability, general methods adopted to develop artificial anti-wetting surfaces, existing challenges, and objectives behind this thesis work. **Chapter 2** demonstrates the strategic use of a catalyst-free 1,4-conjugate addition reaction between distinct and strategically selected small molecules allowed to prepare an active deposition solution with prolonged shelf-life in various and commonly used reaction media to derive optically transparent superhydrophobic coating. **Chapter 3** introduces a covalent cross-linking chemistry between selected reactants to achieve tolerant and hard superhydrophobicity. **Chapter 4** demonstrates the design of chemically functionalizable coatings with a combination of a physically unclonable porous topography and distinct physiochemical properties (e.g., fluorescence, water wettability, and water adhesion) obtained through orthogonal chemical modifications (i.e., 1,4-conjugate addition reaction and Schiff-base reaction at ambient conditions) for multilevel anti-counterfeiting application. **Chapter 5** accounts for the utilization of a crystalline comb-like polymer to derive a non-fluorinated, substrate-independent, and self-healable amphiphobic solid slippery coating following a simple and scalable fabrication process. **Chapter 6** provides a comprehensive summary of the presented work and a future perspective of this discussed research work.

Chapter 1: Introduction

Nature has been the perennial source of inspiration for human progress and development, and drawing inspiration from nature is evident in the literature.^{1,2} One of the widely studied natural phenomena that have gained significant attention is unique wetting behaviour.^{3,4} Wetting refers to the process of interaction between a liquid and a solid surface and is a common phenomenon found in our daily lives, agriculture, industry, etc. Non-wettable surfaces, known as liquid-repellent surfaces, have drawn enormous interest in the scientific community due to their wide range of applications in various fields, such as oil-water separation, biomedical applications, electrochemical applications, water harvesting, anti-icing, energy conversion, droplet transport, etc. The study of superhydrophobicity, inspired by the extremely water-repellent properties of lotus leaf, is one of the earliest research focuses on the topic of liquid repellence, and detailed investigations revealed the presence of hierarchal roughness covered with low surface energy wax-made material (Figure 1A, 1C, 1E). The wettability of this type of rough surface featuring a high water contact angle ($>150^\circ$) and low roll-off angle ($<10^\circ$) has been explained theoretically by the Cassie-Baxter model. According to this model, air remains trapped in the grooves of the microporous structure, forming an air pocket. When a beaded water droplet wets the rough solid surface, the apparent solid-water interface comprises of solid-water interface and air-water interface, considered as heterogenous wettability. Such interfaces are formally classified as non-adhesive superhydrophobic interfaces. Unlike lotus leaf, superhydrophobic surfaces inspired by rose petals (Figure 1B, 1D, 1E) exhibit superhydrophobicity with a high roll-off angle ($>10^\circ$), referred to as adhesive superhydrophobicity. Taking inspiration from nature, various methods have been introduced in the literature to develop artificial

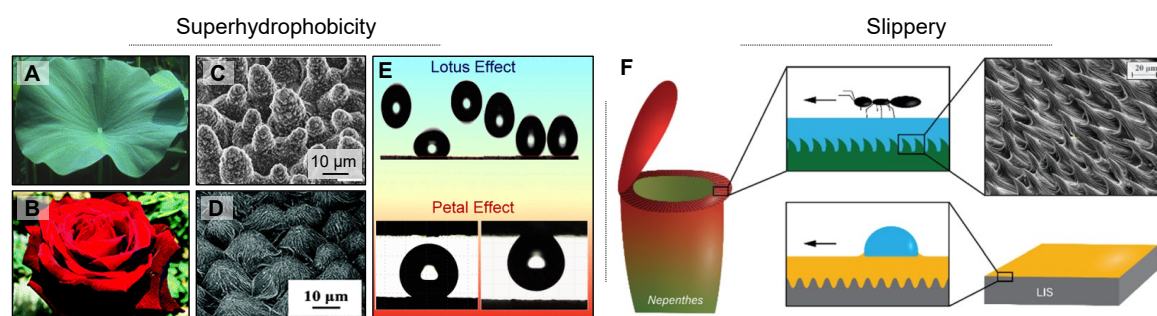


Figure 1: A-D) Photographs (A, B) and SEM (C, D) images of superhydrophobic lotus leaf (A, C) and rose petal (B, D). Reproduced with permission from *ACS Appl. Mater. Interfaces*, 2017, **9**, 8393–8402. Copyright 2017, American Chemical Society F) Schematic depiction of water layer trapping within the peristome of Nepenthes pitcher plant creates a slippery surface, resulting in sliding of ants and Lubricant-infused slippery surfaces. Reproduced with permission from *Chem. Soc. Rev.*, 2020, **49**, 3688–3715. Royal Society of Chemistry, Copyright 2020.

superhydrophobic interfaces. But in contrast to water, low surface tension liquids such as organic solvents and oils can readily wet superhydrophobic interfaces by penetrating into the micro-nano grooves of the rough solid surface. To achieve both oil and water repellence, often a complex topography with re-entrant surface curvature and fluorinated chemical modification is adopted. Developing such complex topography on a large scale is difficult, and the use of fluorinated chemicals is environmentally toxic. To address this limitation, a novel approach has been developed, taking inspiration from *Nepenthes* pitcher plant-inspired, to design lubricant infused slippery surfaces with excellent non-wettable performance. Despite significant progress in the field of liquid-repellent interfaces, poor durability and robustness continue to remain a challenge for real-life applications. Mechanical damage of surface architectures and exposure to chemically abrasive conditions result in the deterioration of the liquid repellence of superhydrophobic surfaces, while slippery surfaces lose their liquid repellence due to the

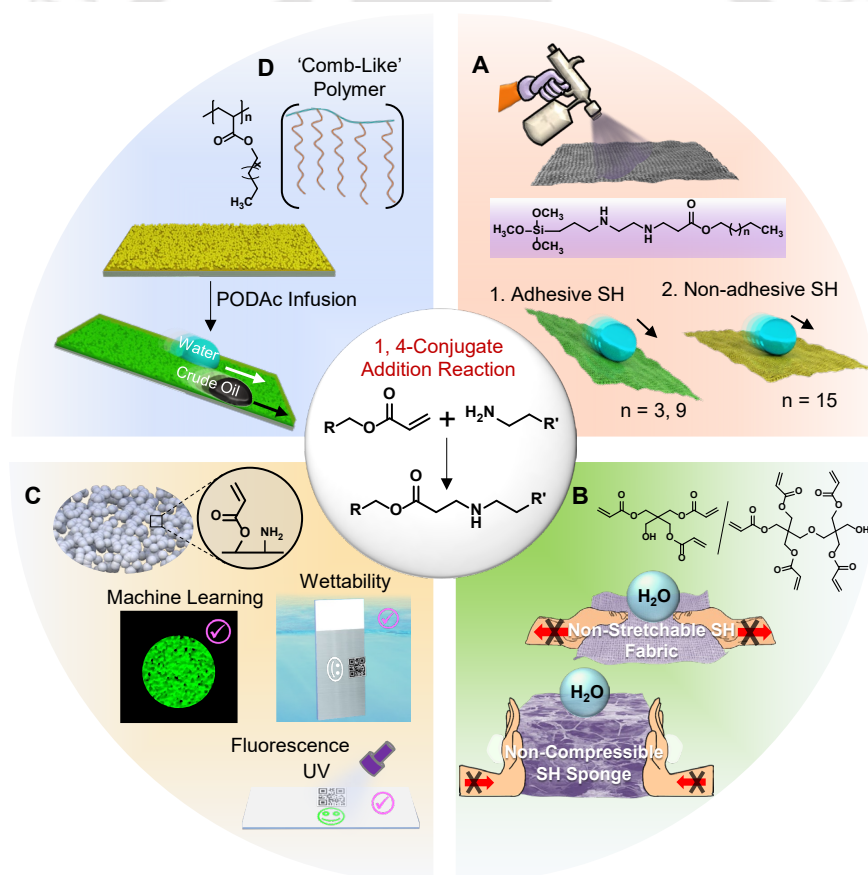


Figure 2: Schematic illustration of the utilization of 1, 4-conjugate addition reaction for developing different liquid repellent polymer coated surfaces, including — A) tailored superhydrophobicity (SH) on fibrous and porous substrates, B) customization of mechanical properties of stretchable and compressible substrates with enhanced durability, C) dual chemically functionalizable porous polymeric coating for multilevel anti-counterfeiting application, D) solid lubricant infusion into the porous network for developing amphiphobic coating.

loss of infused liquid lubricant. To improve the robustness and durability of superhydrophobic surfaces, several approaches have been adopted, such as designing special surface structures, densely and close-packed nanostructures, self-similar rough structures, using hard materials, etc. However, these earlier reported approaches lacked the ability to associate other important properties— including mechanical property, water adhesion, water wettability, etc. Secondly, patterns of extremes of water wettability have been investigated to demonstrate anti-counterfeiting applications, where selective infiltration of water reveals invisible patterns upon exposure to water. However, the major limitation of this approach is the infiltration of water in hydrophilic areas which compromises its self-cleaning ability and immediate disappearance of hidden information. To avoid this issue, the design of a self-cleanable anti-counterfeiting interface with the ability to erase hidden information would be more promising for realistic application. Additionally, slippery surfaces are prepared by infusing liquid lubricant into a chemically inert hydrophobic porous matrix. But these surfaces often suffer from the leaching of infused lubricant resulting in the loss of liquid repellence. Moreover, designing a stable and dry slippery interface through a facile scalable fabrication process is extremely rare in existing literature.

To address these current challenges, in this thesis work, I have utilized a facile and catalyst-free 1,4-conjugate addition reaction between amine and acrylate functional groups of selected small molecules to develop robust and durable liquid-repellent interfaces (Figure 2). This facile approach was exploited to achieve superhydrophobic coating for potential applications in water remediation, anti-fouling, self-cleaning, etc (Figure 2A). A covalently cross-linked gelation process is introduced utilizing a 1,4-conjugate addition reaction between selected non-fluorinated reactants to customize the mechanical property and wettability of the selected deformable and stretchable substrates at ambient conditions (Figure 2B). Moreover, a dual chemically functionalizable porous polymeric coating was prepared utilizing a different sol-gel conversion process and subsequent post-chemical modulations were employed to associate fluorescence superhydrophobicity and tailored water adhesion. This chemically functionalizable polymeric coating with a combination of physically unclonable porous topography and distinct physiochemical properties is utilized to develop a multilevel anti-counterfeiting interface (Figure 2C). Additionally, a porous polymeric network was prepared using the same sol-gel chemistry with a variation in morphology. Further, a non-fluorinated, self-healable, substrate independent, amphiphobic solid slippery coating was achieved by infusing a crystalline 'comb-like' solid lubricant into this porous matrix (Figure 2D).

Chapter 2: Small Molecules based Tolerant Superhydrophobic Coating on Fibrous and Porous Substrates

In the past, different approaches were adopted to prepare superhydrophobic interfaces for demonstrating various prospective applications, where different polymers or nanomaterials are associated to achieve appropriate hierarchical topography and essential chemistry. The commonly used deposition solutions consisting of polymer or nanomaterials prepared in a

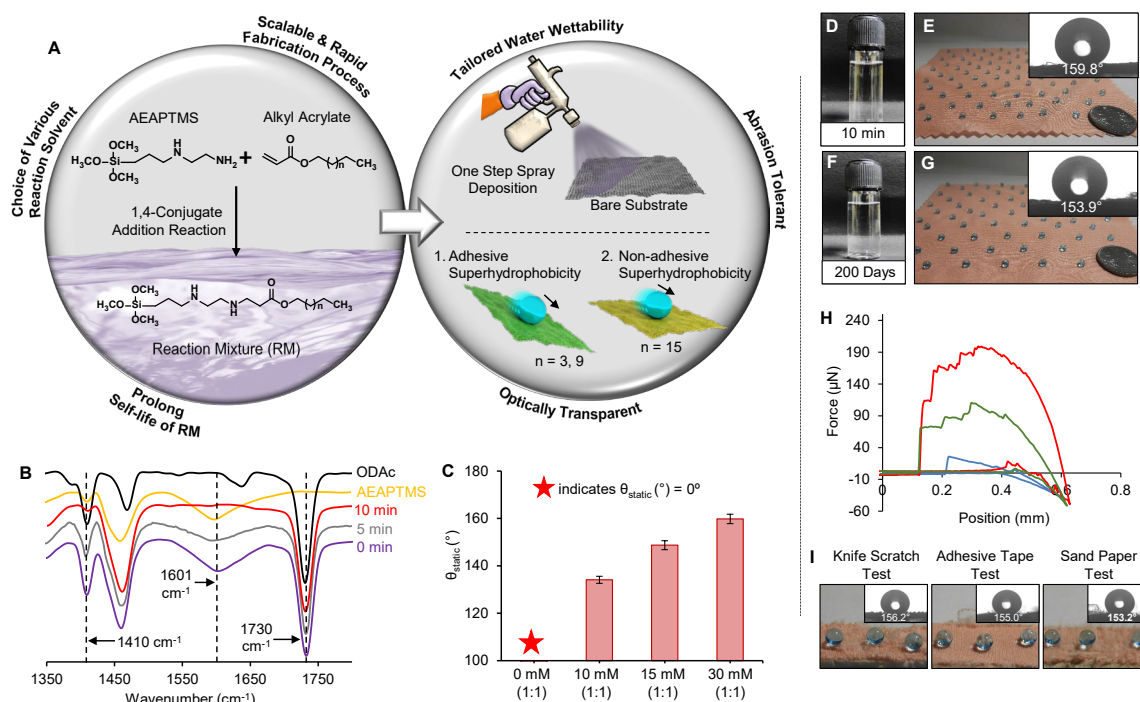


Figure 3: A) Schematic depicting the fabrication of an abrasion tolerant, optically transparent, tailored water wettability achieved through the rational use of 1,4-conjugate addition reaction between selected small molecules—alkyl acrylate and [3-(2-Aminoethylamino)propyl] trimethoxysilane (AEAPTMS) in a wide range of volatile organic solvents under ambient conditions. B) Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectra for the individual solution of selected small molecules—octadecyl acrylate (ODAc, black) and AEAPTMS (yellow) and the reaction mixture (1:1) of ODAc and AEAPTMS in ethanol at regular time intervals, including 0 min (blue), 5 min (green) and 10 min (red). C) Plots accounting for the changes in static contact angle on the synthesized coatings that were prepared by varying different molar concentrations of selected reactants, where the molar ratio of reactants kept at 1:1. D, F) Photographs of the reaction mixture of ODAc and AEAPTMS in ethanol after ageing it for 10 min (D) and 200 days (F). E, G) Digital image and contact angle image (inset) of beaded water droplets on the coated fabric, where the reaction mixture spray deposited after storing for 10 min (E) and 200 days (G). H) Adhesion force data for the coatings that were individually derived from reaction mixtures containing different acrylates (hexyl acrylate, red; lauryl acrylate, green; ODAc, blue), respectively. I) Digital images and contact angle images (inset) of the beaded water droplets after knife test, adhesive tape peeling test, and sandpaper abrasion test. (*Chem. Eng. J.*, 2022, **430**, 132597)

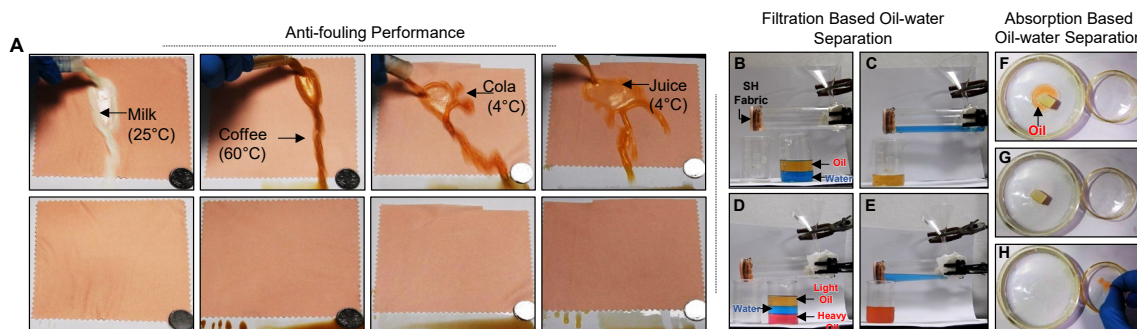


Figure 4: A) Photographs depicting the antifouling performance of superhydrophobic coating with the stream of milk, hot (60 °C) coffee, cold (4 °C) cola and cold (4 °C) juice. B-E) Digital images illustrating the selective collection of oil from the oil-water mixtures. F-H) Illustrating selective absorption and collection of the floating oil droplet on aqueous phase by the superhydrophobic melamine sponge. (*Chem. Eng. J.*, 2022, **430**, 132597)

specific solvent have poor shelf-life. Moreover, the unavailability of robust and optically transparent superhydrophobic coating following a scalable, rapid, and single-step deposition process remained a bottleneck problem for its various prospective and relevant applications in real-world scenarios. In this current design, two different types of small molecules, including 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS) and alkyl acrylate, are unprecedentedly reacted through 1,4-conjugate addition reaction to prepare an active deposition solution for developing a) fluorine-free b) abrasion tolerant and c) optically transparent (99.2%) superhydrophobic coating following d) a simple, rapid, and single step deposition process, as shown in Figure 3A.

The selected reactants were mixed in the molar ratio of 1:1 in ethanol at ambient conditions, and as expected, amine groups of AEAPTMS spontaneously reacted with the acrylate moiety of octadecyl acrylate (ODAc) as characterized through standard Fourier transform infrared attenuated total reflectance spectra (FTIR-ATR) analysis (Figure 3B). During the 1,4-conjugate addition reaction between amine and acrylate groups, FTIR-ATR peaks at 1410 cm^{-1} corresponding to C–H deformation of β -carbon of vinyl group of ODAc significantly reduced with respect to carbonyl group stretching at 1730 cm^{-1} . Next, the reaction mixtures having different molar concentrations (10 mM to 30 mM) were spray deposited on a polyurethane-based inherently hydrophilic fibrous substrate. On increasing the concentration of reaction mixtures (the molar ratio of reactants kept at 1:1), the spray deposited coating displayed enhanced water wettability (from 134° to 159°), as shown in Figure 3C. At the concentration of 30 mM of each of the selected reactants (AEAPTMS and ODAc), the deposition solution-I (denoted as DS-1) was spray deposited to achieve superhydrophobicity with a water contact

angle of $\sim 159^\circ$ (Figure 3D, E). Thereafter, the same reaction mixture that was stored in ambient conditions for 200 days was spray deposited (Figure 3F), and the coating displayed superhydrophobicity with WCA above 150° (Figure 3G). Next, the adhesive interaction between the bio-inspired coating and beaded water droplet was modulated through a rational selection of alkyl acrylates during the preparation of the reaction mixture. The deposition solutions were prepared by individually mixing hexyl acrylate (HAc; 30 mM) and dodecyl acrylate (DDAc, 30 mM) with AEAPTMS (30 mM), denoted as DS-2 and DS-3. The separate spray deposition of the DS-2 and DS-3 provided tailored superhydrophobicity. The adhesive forces between the beaded droplet and the superhydrophobic coatings that were derived from DS-2 and DS-3 were found to be 204 μN (red) and 104 μN (green), respectively. The superhydrophobic coating derived from DS-1 (having ODAc) displayed an adhesive force of 24 μN (blue) (Figure 3H). Thus, the adhesive force gradually decreased on the association of higher analogues of HAc. To investigate the robustness of the synthesized non-adhesive superhydrophobic coating, various standard and practically relevant abrasive tests such as knife scratch test, adhesive tape peeling test, and sandpaper abrasion test were performed on the freshly prepared bio-inspired coating. The water droplets beaded on the physically damaged interface with a static WCA $>150^\circ$ (Figure 3I).

The embedded superhydrophobic coating prevented the wetting of the coated interface by streams of milk, coffee, cola, and juice, as shown in Figure 4A. Next, the superhydrophobic fibrous interface was extended as a selective oil-filtrating membrane for performing the gravity-driven and environment-friendly oil/water separation. The oil phase was selectively filtrated through the superhydrophobic interface and collected in an individual container that was placed under the prototype (Figure 4B-E). Next, the superhydrophobic MF sponge was extended for selective absorption-based oil-water separation (Figure 4F, G). Further, the application of manual compressive strain led to the recovery of the absorbed oil phase, as shown in Figure 4H. Such a design of bio-inspired coating is unprecedented in the literature and would be useful for various relevant applications in ‘real-world’ scenarios.

Chapter 3: Design of ‘Tolerant and Hard’ Superhydrophobic Coatings to Freeze Physical Deformation of Deformable Substrates

Superhydrophobic coatings on inherently soft fibrous and/ or spongy substrates have shown immense potential for widespread application—including oil–water separation, smart strain sensors, temperature and pressure sensing, anti-blood repellence, etc. Recently, a few

approaches were introduced to prepare non-compressible superhydrophobic monoliths/concrete, which could be beneficial for developing smart architectures, ships, aircraft, etc. Thus, the design of both deformable and non-deformable superhydrophobic materials/interfaces is of potential interest for various relevant applications. Earlier, numerous distinct and multistep approaches were adopted to prepare non-deformable monoliths, compressible sponges and stretchable superhydrophobic interfaces. Interestingly, the design of a common and single-step fabrication process to prepare two distinct and tolerant superhydrophobic coatings that would either allow or restrict the physical deformation of the underlying highly compressible and stretchable substrates is yet to be introduced in the literature. In this work, I reported a facile 1,4-conjugate addition reaction under ambient conditions between selected reactants, i.e. [3-(2-aminoethylamino)propyl] trimethoxysilane (AEAPTMS) and octadecyl acrylate (ODAc), in the presence of a selected crosslinker

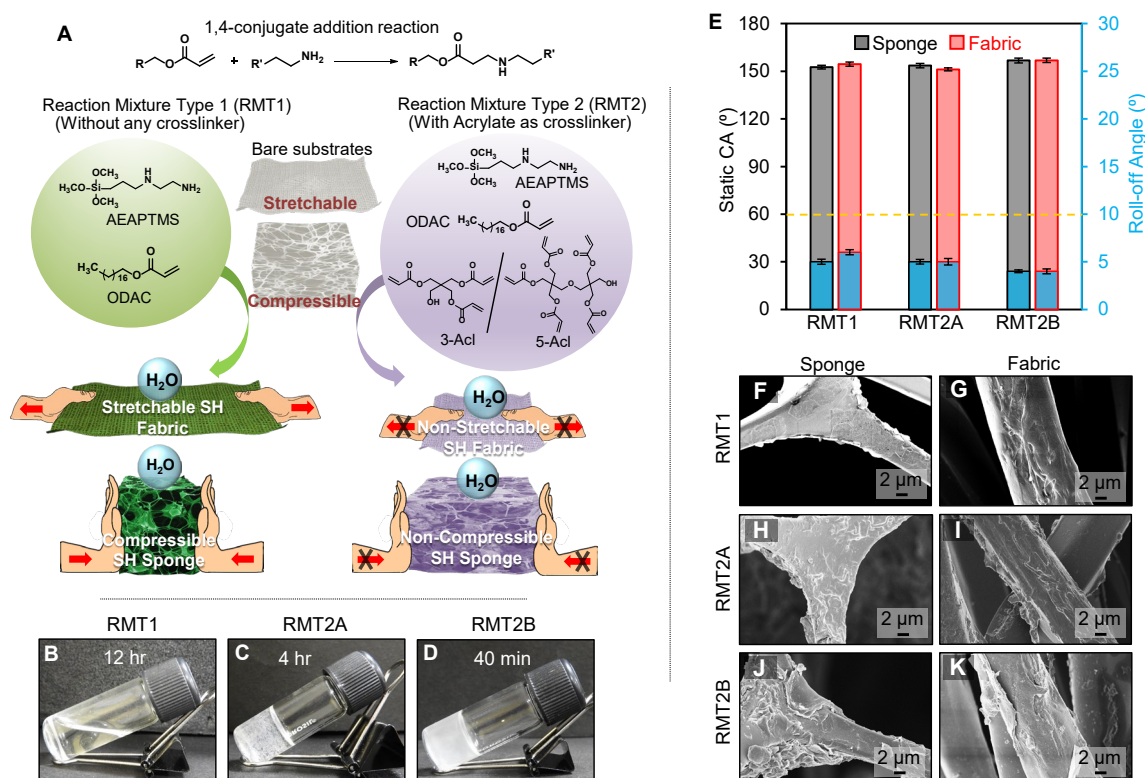


Figure 5: A) A schematic illustration for the preparation of both deformable and non-deformable superhydrophobic materials in the absence and presence of different crosslinkers following 1,4-conjugate addition reaction between acrylate and amine functional groups via a simple dip-coating method. B-D) Photographs depicting the sol-gel conversion process of different reaction mixtures. E) Bar plot demonstrating the static contact angles and roll-off angles of materials (melamine sponge, black; polyurethane fabric, red) coated with three reaction mixtures – RMT1, RMT2A and RMT2B. F-K) FESEM images of substrates coated with the three different reaction mixture solutions RMT1 (sponge, F; fabric, G), RMT2A (sponge, H; fabric, I) and RMT2B (sponge, J; fabric, K). (*Mater. Horiz.*, 2021, **8**, 2717–2725)

molecules [pentaerythritol tri-acrylate (3-Acl) or dipentaerythritol penta-acrylate (5-Acl)] to develop nondeformable (compressible/stretchable) superhydrophobic coatings on selected soft and deformable underlying substrates, i.e., polyurethane fabric (highly stretchable) and melamine formaldehyde sponge, respectively, as shown in Figure 5A. In absence of a crosslinker, the coating, as described in the last chapter, failed to display such mechanical property.

In the current design, two distinct small molecules and appropriate crosslinkers were strategically used to prepare two types of reaction mixtures: reaction mixture type 1 (RMT1, comprised of AEAPTMS and ODAc, similar to the last chapter but comprising of different concentration of reactants) and reaction mixture type 2 [RMT2: comprised of AEAPTMS and ODAc and the selected crosslinker (3-Acl or 5-Acl)]. The physical states of these two types of reaction mixtures were observed to be completely different after mixing the selected reactants under ambient conditions. While RMT1 remained transparent liquid even after 12 h of mixing of AEAPTMS and ODAc, RMT2 (A/B) comprised of different crosslinkers (3-Acl/ 5-Acl)

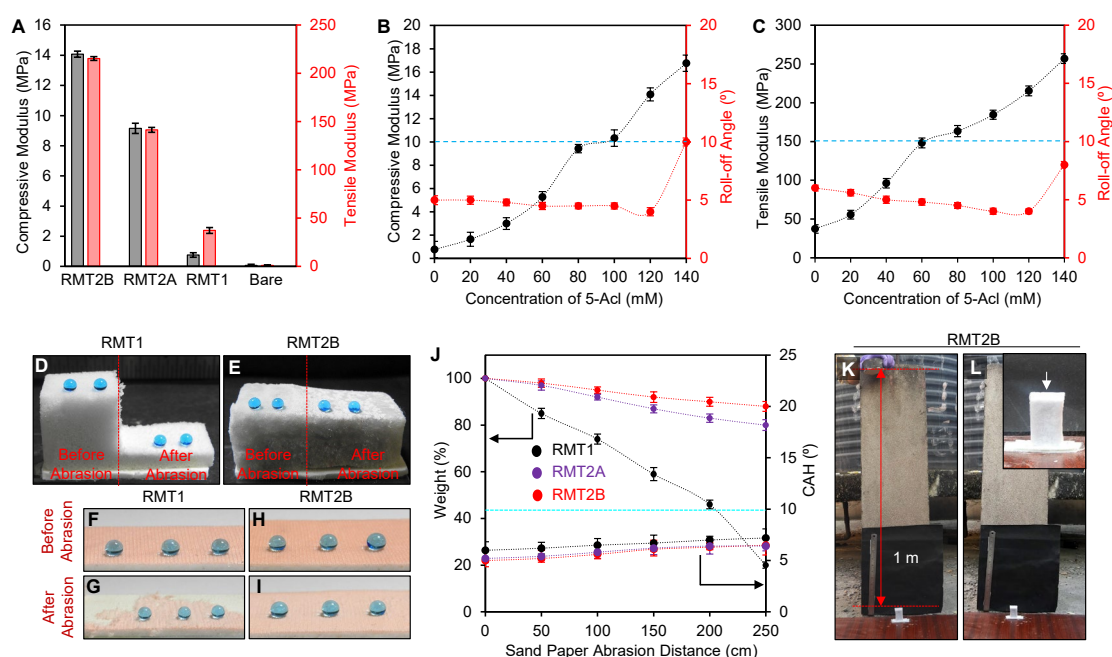


Figure 6: A) Bar plot comparing the compressive and tensile modulus of bare and different reaction mixture (RMT1, RMT2A and RMT2B) coated melamine sponge and polyurethane fabric. B, C) Plot illustrating the change in mechanical property and wettability of RMT2B coated substrates upon varying the concentration of cross-linker 5-Acl in the reaction mixture. D-I) Photographs of RMT1 and RMT2B coated sponge (D, E) and fabric (F-I) before and after sandpaper abrasion. J) Plot demonstrating the change in weight (%) and contact angle hysteresis (CAH) of sponge coated with three different reaction mixtures upon increasing the sandpaper abrasion distance. K, L) Photographs showing the impact of 1 kg weight RMT2B coated sponge from 1 m distance. (*Mater. Horiz.*, 2021, **8**, 2717–2725)

formed gel at different times, specifically, 4 h and 40 min depending on the type of crosslinker 3-Acl and 5-Acl respectively, as shown in Figure 5B-D. Subsequently, the three different reaction mixtures (RMT1, RMT2A and RMT2B) were individually deposited on the selected stretchable fabric (polyurethane-based) and compressible sponge (melamine formaldehyde). All three reaction mixtures that provided respective coatings were efficient in displaying the desired superhydrophobicity with static water contact angles (WCAs) above 150° and roll-off angles below 10° , as shown in Figure 5E. Further, field emission scanning electron microscope (FESEM) images (Figure 5F-K) of all coated substrates confirm the presence of random rough features on the selected substrates, suggesting the deposition of the respective reaction mixtures. Further, the compressive modulus and tensile modulus of the melamine formaldehyde sponge and polyurethane fabric were measured before and after the individual dip-coating in the selected reaction mixtures—RMT1, RMT2A and RMT2B. The enhancement of the compressive and tensile modulus was found to be maximum (14.08 MPa and 215.33 MPa) for the RMT2B coated substrates — whereas a significantly less (0.755 MPa and 37.27 MPa) increment was noted for the RMT1 coated substrates compare to mechanical properties of the native substrates, as shown in Figure 6A. Next, a series of reaction mixtures were prepared by gradually increasing the concentration of 5-Acl from 0 mM to 160 mM, where the other two reactants were AEAPTMS and ODAc. The individual deposition of these reaction mixtures on the spongy substrate and stretchable fabric yielded superhydrophobic interfaces (static WCAs above 150° and roll-off angles $\leq 10^\circ$)—with gradually increasing compressive modulus (for the selected sponge, Figure 6B) and tensile modulus (for the stretchable fabric; Figure 6C) depending on the content of 5-Acl without any significant change in wettability. Next, the durability of the prepared coatings and their impact on preventing the physical disintegration of the selected soft substrates were studied by adopting some standard and widely accepted abrasive exposure and impact tests. Exposure to abrasive sandpaper with an externally applied pressure of 25 kPa, the physical integrity and wettability of RMT2B coated substrates remained intact with minimal mass loss, whereas significant physical erosion and mass loss were noted for the RMT1-coated substrates as shown in Figure 6D-J. The RMT2B coated sponge was efficient in tolerating the impact of dropping the same 1 kg load from 1 m—without causing any noticeable physical damage to the material, as shown in Figure 6K, L. Hence, this simple and elegant chemical approach not only controlled the mechanical properties of the porous and fibrous soft substrates under ambient conditions—but also provided highly tolerant superhydrophobicity— which likely leads to various outdoor applications.

Chapter 4: Design of a Self-Cleanable Multilevel Anticounterfeiting Interface through Covalent Chemical Modulation

Counterfeit products have posed a significant threat to consumers' safety and the global economy. To address this issue, extensive studies have been exploring the use of coatings with unclonable, microscale features for authentication purposes. However, the ease of readout, and the stability of these features against water, deposited dust, and wear, which are required for practical use, remain challenging. This chapter demonstrates the design and synthesis of a self-cleaning coating with adhesive and non-adhesive superhydrophobic patterns that are invisible in the air but are visible underwater to the naked eye, allowing for instrument-free information decryption. Furthermore, the strategic combination of adhesive and non-adhesive water wettability, optical properties, and unclonable microscale topography would enable the development of a new class of physically unclonable surfaces for multilevel information encryption and decryption. First, I have synthesized and modified a dual chemically functionalizable porous polymeric coating using a 1,4-conjugated addition and Schiff-base reaction to enable multilevel authentication of a chemically modulated pattern, as shown in Figure 7A-D. The porous and chemically functionalizable coating was prepared through a 1,4-conjugate addition reaction between branched polyethyleneimine (BPEI) and dipentaerythritol penta-acrylate (5-AcI) in heptanol. This coating has undergone spatial selective covalent modification with glutaraldehyde (Glu) through imine bond formation to introduce fluorescence. Eventually, the Glu-modified pattern appeared only under UV light (365 nm) exposure but not under visible light, as evidenced by the word 'REAL' in Figure 7E-G. Next, we demonstrated machine learning-aided anticounterfeiting with images of the fluorescence spots obtained using a fluorescence microscope. Post-chemical modification of the coating with octadecylamine (ODA) gives rise to non-adhesive superhydrophobicity, whereas successive modification with 2-hydroxy acrylate (HA) and ODA (denoted as HA@ODA) resulted in an adhesive superhydrophobicity. The adhesive force on the HA@ODA-modified coating (104 μN) was almost two times that of the ODA-modified coating (57 μN), as shown in Figure 7H. Hence, the trapped air in the ODA-modified coating resulted in a highly shiny appearance through the internal reflection of light after submerging the coating underwater, whereas the HA@ODA-modified coating appeared less shiny, as shown in Figure 7I. As a result, a smiley face pattern created through spatially selective modification with HA@ODA is made visible upon exposure to water, as demonstrated in Figure 7J, K. In the final experiment, I combined the fluorescence and water adhesion characteristics into a single

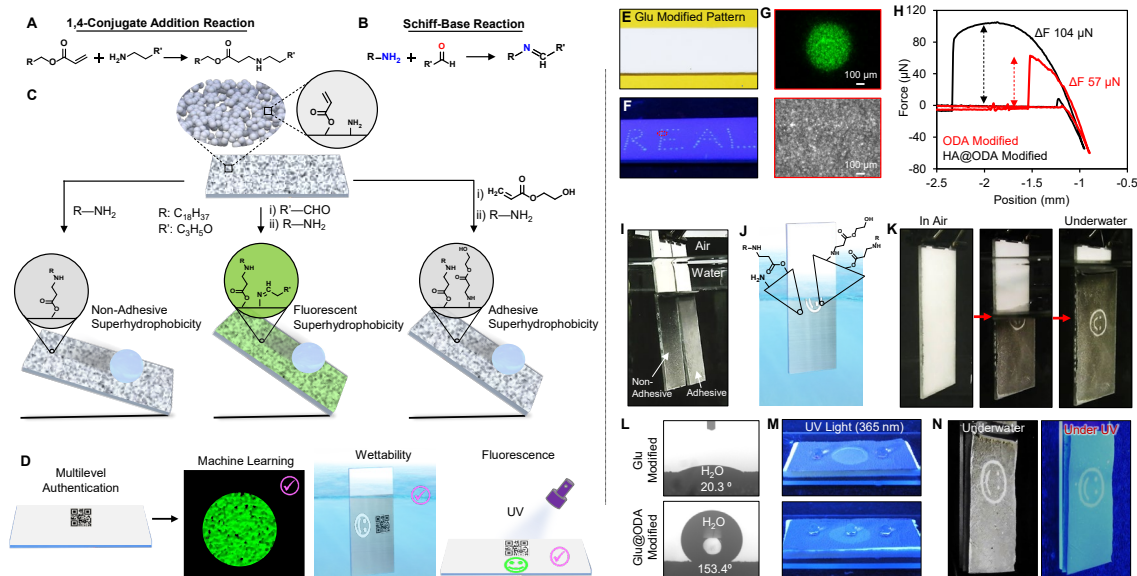


Figure 7: A-B) 1,4-conjugate addition reaction (A) between a primary amine and acrylate functional groups and the Schiff base reaction (B) between an aldehyde and primary amine functional groups. C) Scheme of different post-chemical modifications for non-adhesive, adhesive, and fluorescent superhydrophobicity. D) Schematic depiction of three distinct authentication steps to identify the legitimacy of a quick response (QR) code on the porous polymeric coating. E, F) Photographs of 'REAL' patterned coating through selective modification with glutaraldehyde under visible light (E) and UV illumination (365 nm, F). G) Fluorescence and phase contrast micrographs of one region of the 'REAL' pattern in (F). H) Adhesion force of a 5 mL water droplet on ODA and HA@ODA-modified adhesive coating. I) Photograph depicting the appearance of the shiny interfaces of ODA and HA@ODA-modified coatings underwater denoted as non-adhesive and adhesive, respectively. J, K) Schematic illustration (I) and corresponding photographs (J) of the appearance of an underwater smiley pattern created through ODA and HA@ODA modification. (*Mater. Horiz.*, 2023, **10**, 2204–2214)

coating for multilevel encryption and orthogonal decryption with the naked eye. The spatially selective dual modifications of the coating with Glu and ODA (denoted as Glu@ODA) conferred both fluorescence and adhesive superhydrophobicity (Figure 7L, M). The smiley pattern on the coating achieved through spatially selective modulation using Glu and ODA allowed the co-association of water adhesion and UV responsiveness in the same location, and the pattern remains invisible under visible light in the air can be read when the surface is submerged underwater or when it is exposed to UV light (Figure 7N). In summary, I reported the design and synthesis of physically unclonable coatings that enable multilevel anticounterfeiting by chemical and spatial modification. Notably, the encryption can be independently authenticated by following one or both, an automated machine-learning process and an instrument free, naked-eye readout technique.

Chapter 5: Designing a Network of Crystalline Polymers for a Scalable, Nonfluorinated, Healable and Amphiphobic Solid Slippery Interface

The fluorinated-liquid infused amphiphobic slippery interfaces exhibiting superior sliding of the beaded oil/water droplets often suffer from durability and contamination issues. In this chapter, a non-fluorinated, substrate-independent, and self-healable amphiphobic solid slippery coating was developed following a simple and scalable fabrication process (Figure 8A-F). The strategic use of 1,4-conjugate addition reaction between selected reactants (polyethyleneimine, branched (BPEI; Mw ~ 800 Da) and dipentaerythritol penta-acrylate (5 Acl)) provided the porous polymeric coating to infuse selected lubricant—i.e., ‘comb-like’ polymer having variable hydrocarbon side chain, as shown in Figure 8D, E. In the current design, firstly, a thick (4.86 μm) and porous polymeric coating was developed through a 1,4-conjugate addition reaction between amine and acrylates by the spray depositing the reaction mixture of BPEI and

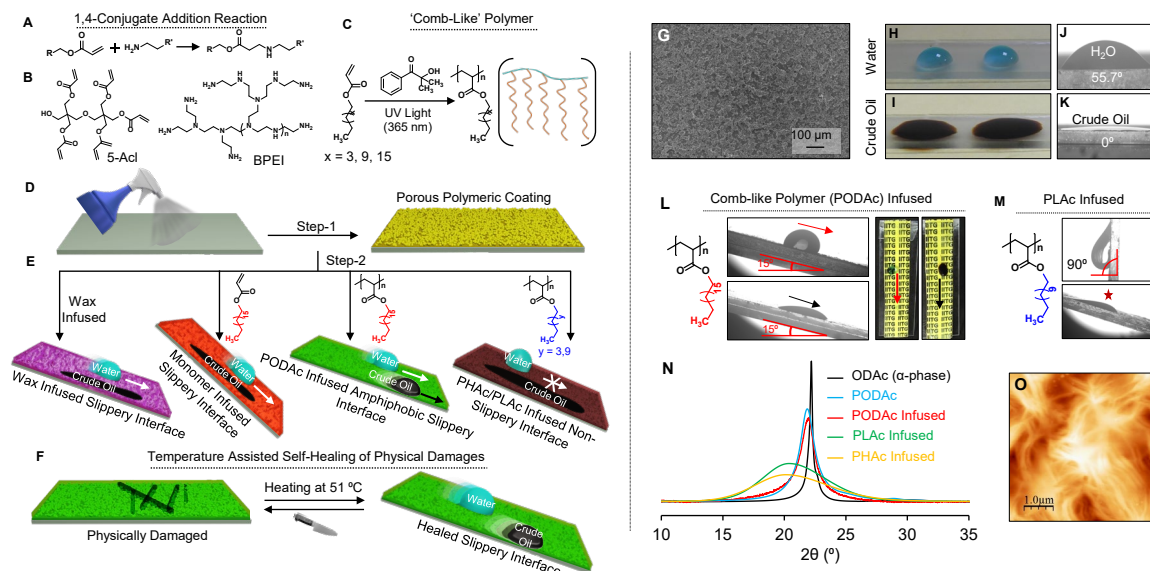


Figure 8: A) Schematic presentation of the 1,4-conjugate addition reaction between amine and acrylate functional groups. B) Chemical structure of dipentaerythritol penta-acrylate (5-Acl) and branched polyethyleneimine (BPEI). C) Schematic illustration of photopolymerization of octadecyl acrylate monomer (ODAc) in the presence of a radical. D, E) Schematic diagram illustrating the two-step fabrication procedure of different slippery coatings. F) Schematic illustrating the temperature-assisted self-healing of physically damaged amphiphobic solid slippery coating. G) FESEM images of porous polymeric coating. H-K) Photographs and contact angle images of beaded water and crude oil droplets on porous coating. L) Sliding angle and photographs of the polyoctadecyl acrylate (PODAC)-infused coating showing the sliding of both water and crude oil. M) Demonstrating the pinning and spilling of beaded water (J) and crude oil (K) droplets, respectively, on the polylauryl acrylate (PLAc) infused coating. N) Graph showing the XRD peaks of ODAc (black), PODAc (Blue) and coatings infused with PODAc (red), PLAc (green), and PHAc (yellow). O) AFM image of PODAc-infused coating. (*Angew. Chem. Int. Ed.*, 2022, **61**, e202116763)

5-Acl at ambient conditions, as shown in Figure 8G. The prepared porous polymeric coating was found to be inherently hydrophilic and superoleophilic—where the droplets of water and crude oil beaded with contact angles of $\sim 56^\circ$ and 0° , respectively (Figure 8H-K). Secondly, the infusion of a selected and crystalline (Figure 8C) "comb-like" polymer (i.e., poly(octadecyl acrylate) (PODAc), $M_n \approx 98600$ Da) in the same porous polymeric coating resulted in a highly efficient amphiphobic solid-slippy interface. The spontaneous sliding of both the beaded droplets of water (volume of $30\ \mu\text{L}$) and crude oil (volume of $10\ \mu\text{L}$) with a sliding angle (SA) of 15° was noted on the "comb-like" polymer infused coating, as shown in Figure 8L. Interestingly, the same porous polymer coating infused with other "comb-like" polymers having shorter hydrocarbon side chains poly(lauryl acrylate) (PLAc) absolutely failed to provide slippy coating, rather the beaded droplets of water and crude oil were pinned (at 90° tilting angle) and spilled, respectively, as shown on Figure 8M. Further, the X-ray diffraction (XRD) pattern was analyzed to understand such differences in slippy properties for different comb-like polymers. The PODAc infused porous polymeric coating displayed an X-ray diffraction peak (at 2θ of 22.08°) corresponding to the hexagonal packing with a spacing of $4.02\ \text{\AA}$, which resembled the crystalline α phase (hexagonal packing) of respective monomer (ODAc, Figure 8N), whereas no such sharp XRD peak was noted for other comb-like polymer (PLAc) infused porous polymeric coatings, as shown in Figure 8N. Furthermore, the highly magnified AFM images revalidated the presence of a fibrous topography on the solid slippy interface (Figure 8O). Further, the prepared PODAc infused solid slippy interface was highly efficient at sliding a wide range of beaded droplets of liquids, including water, polar (ethanol, 1-propanol, 1-hexanol, DMSO, DMF), and non-polar (decane, dodecane, diiodomethane) organic solvents and edible (vegetable oil), motor, engine (petrol, diesel, kerosene) oils and crude oil, as shown in Figure 9A. The selected and solid comb-like polymer, PODAc, exhibits reversible phase transition behaviour upon heating and melted on heating at $\approx 51^\circ\text{C}$, as determined from differential scanning calorimeter (DSC) analysis (Figure 9B). This thermal-assisted phase transition phenomenon was utilized further to restore the liquid repellence of damaged interfaces (Figure 9C). Moreover, the synthesized solid amphiphobic slippy property of the PODAc infused polymeric interface remained unperturbed, even after prolonged (15 days) and continuous exposures at extremes of pH (2 and 12), seawater, river water, UV irradiation (254 nm and 365 nm), as shown in Figure 9D. Another important feature of the current design is its substrate-independent and scalable fabrication process. Thereafter, the amphiphobic solid slippy coating was applied on more relevant substrates, i.e., safety

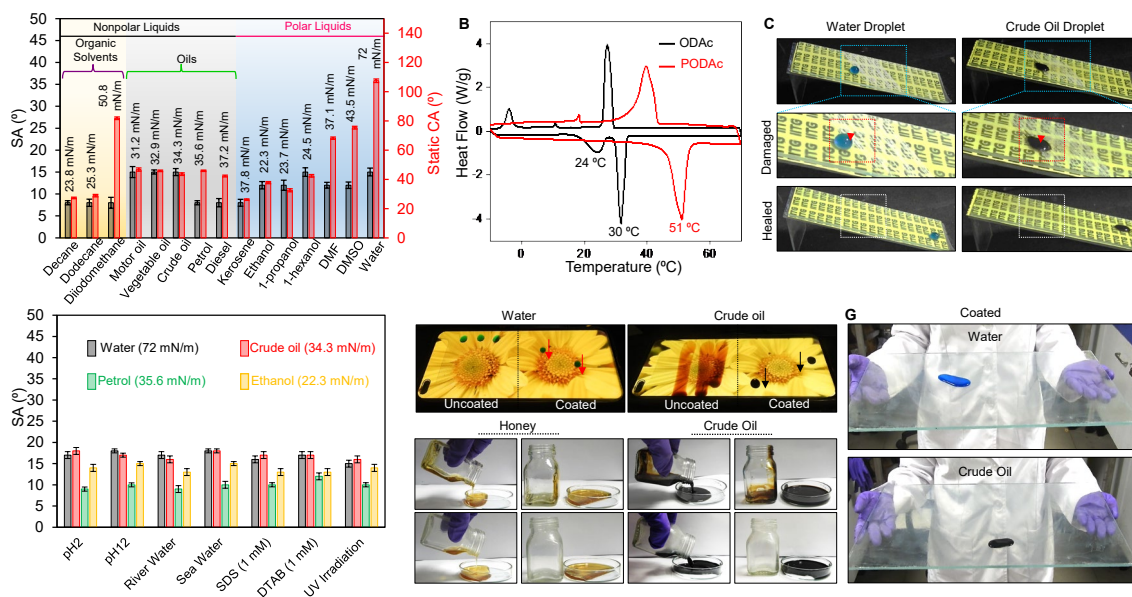


Figure 9: A) Bar plot of sliding angles (SA) and static contact angles of different non-polar and polar liquids with a wide range of surface tension on PODAc-infused coating. B) Graph showing the phase transition temperature of ODAc (black) and PODAc (red) upon heating. C) Photographs illustrating the pinning and sliding of water and crude oil droplet on physically damaged and healed PODAc-infused coating. D) Bar diagram of sliding angles (SA) of water (black), crude oil (red), petrol (green) and ethanol (yellow) on PODAc-infused coating exposed to various harsh chemical environments for 15 days. E) Digital images showing the pinning and sliding of water and crude oil droplets on uncoated and coated regions of tempered glass of a mobile phone, respectively. F) Demonstrating the dispensing of honey and crude oil from an uncoated and a PODAc-infused coated glass bottle, respectively. G) Illustrating sliding of water and crude oil PODAc-infused coated large (1325 cm²) glass objects. (*Angew. Chem. Int. Ed.*, 2022, **61**, e202116763)

glass (often called tempered glass) for cell phone displays and the interior of a glass bottle. Droplets of water and crude oil readily slide on the coated screen protector of a cell phone, as shown in Figure 9E. Honey and crude oil dispensed readily and entirely from the coated glass bottle, as shown in Figure 9F. The results were also compared with uncoated substrates. Further, the simplicity of the fabrication process allowed the derivation of the coating on a large area (1325 cm²) of a glass substrate (Figure 9G).

Chapter 6: Conclusions and Future Directions

In summary, this synopsis report introduces a facile and scalable chemical approach following a simple 1, 4-conjugate addition reaction for designing robust and mechanochemically durable liquid repellent surfaces, including superhydrophobic and slippery surfaces. The mutual reaction between amine and acrylate functional groups of the selected reactants provided a unique deposition solution with a prolonged shelf-life for achieving durable superhydrophobic

coating on various fibrous and porous substrates. This coated substrate was extended to demonstrate its potential for some relevant and outdoor applications, including oil/water separation, controlled and no-loose manipulation of water droplets, etc. Moreover, this 1,4-conjugate addition reaction has been extended further to achieve both tolerant superhydrophobicity and customized mechanical properties in a single step through strategic and controlled addition of appropriate acrylate crosslinkers into the reaction mixture. Subsequently, a dual chemically functionalizable highly porous polymeric coating was prepared following the same chemistry for multi-level anticounterfeiting applications. Next, a porous polymeric coating was used as a matrix to infuse a comb-like polymer as a solid lubricant to design a substrate independent, healable amphiphobic solid slippery coating.

In recent years, superhydrophobic surfaces have gained significant interest in application in various research topics, such as wearable sensors, catalytic electrodes, photothermal manipulation, etc. Underwater vibration sensing has substantial importance in human safety, military defence, environmental protection, disaster prevention, etc. Most of the presented sensing devices lose their efficiency due to hydrophilicity. Hence, the amalgamation of hydrophobicity with these sensing devices will be an important avenue to ensure the working stability and lifetime of the device. Another notable challenge faced by these devices is material flexibility and substrate attachment. In this context, hard and tolerant superhydrophobic materials presented in this synopsis report with the integration of conductivity can be explored in developing underwater vibration sensing devices. Strategic association of conductive materials such as graphene, silver nanowires, carbon nanotubes, polypyrrole, etc, in the reaction mixture described in Chapter 3 would allow the development of conductive and robust superhydrophobic coated substrates in a single step. The mechanical properties and wettabilities of selected substrates can be tuned through the strategic choice of appropriate crosslinkers and hydrophobic molecules. The effect of tailoring mechanical properties and wettabilities on the performance of the sensing device will be an important aspect to explore in future.

Although superhydrophobic surfaces have enormous applications, but mostly reported surfaces are chemically inert in nature. It is always challenging to get superhydrophobicity and chemical reactivity on the same surface. In the past, chemically reactive surfaces have been used to create patterns with heterogeneous wettability, and they have a wide range of applications in energy harvesting, microfluidics, biomedical detection, water harvesting, etc. Hence, the chemically functionalizable porous polymeric coating outlined in this synopsis report consists of residual

amine and acrylate groups and can be used further for selective modification with hydrophilic and hydrophobic molecules for different wettability patterning to showcase relevant practical applications such as in microfluidics, cell culture, microdroplet arrays, etc.

Further, the developed amphiphobic solid slippery coated surfaces discussed in this synopsis report can be used to derive smart windows capable of fine-tuning the solar spectrum exposure and controlling the energy requirement to maintain the temperature of a building. Also, functionalization of slippery surfaces with micro/nano patterns will broaden the scope for applications such as water harvesting, microdroplet arrays, directional transport of liquid, etc. It is challenging to create amphiphilic-amphiphobic patterned interfaces. As a result, designing a chemically reactive amphiphobic solid slippery surface can provide a solution to derive a patterned slippery interface combining amphiphobic and amphiphilic wettabilities through a post-functionalization approach. Therefore, these developed liquid repellent materials exhibit significant versatility and can be used in various areas.

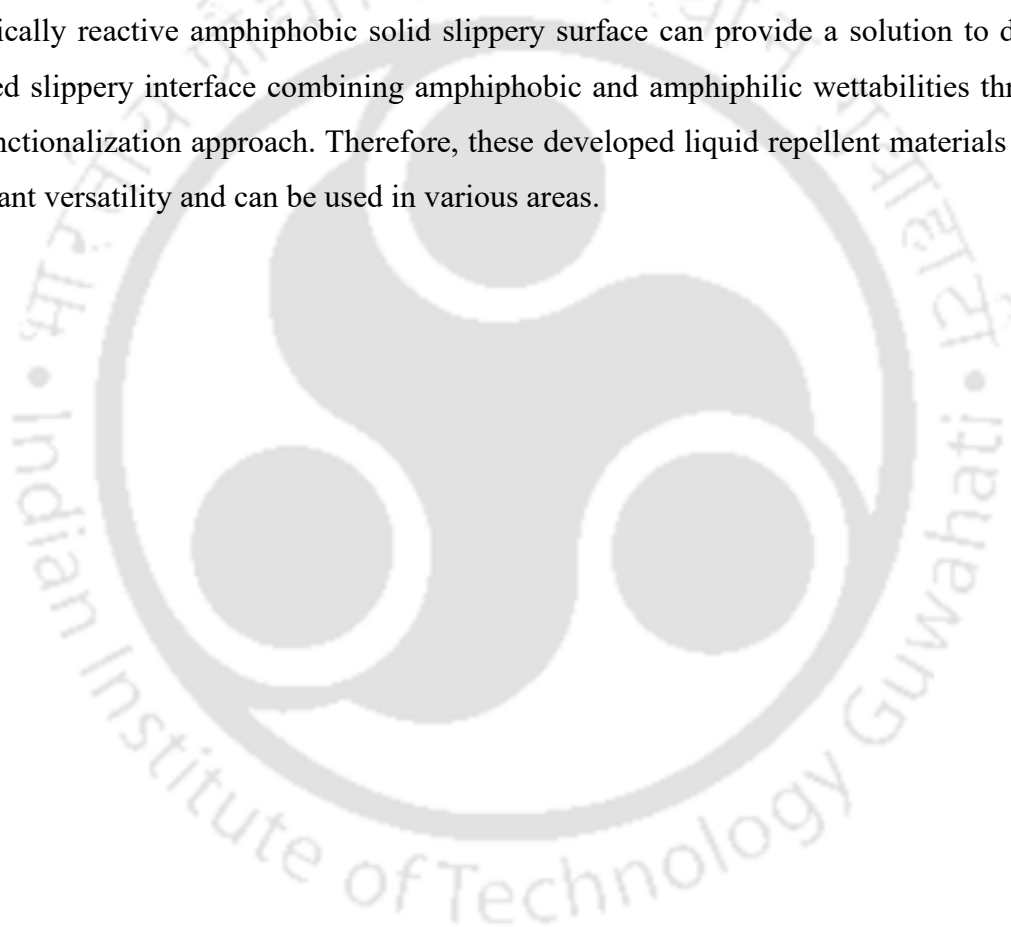


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Chapter 1: Introduction

1.1 Biomimetics: Mimicking Nature for Innovation

Nature has been a great source of inspiration for mankind across various domains, spanning from biology to engineering, design to technology, offering innovative materials and solutions to deal with several challenges.¹⁻⁵ Biomimicry is a process of learning, mimicking, and adapting natural phenomena to find solutions to relevant problems. In this context, engineers and researchers often adopt biomimetic approaches to develop innovative technologies and architectures. There are numerous examples of biomimicry in different domains. For example, birds in flight have been the great source of inspiration behind the discovery of aeroplanes. Leonardo da Vinci was inspired by the flight of birds and created several sketches with the aspiration to design a flying machine, which is now known as aeroplane. Later, Wright brothers got inspired by his research and successfully invented the world's first motor operated aeroplane.^{6,7} Velcro is another example of nature inspired technology. In 1941, a Swiss engineer named George de Mestral invented Velcro after closely observing small burrs of burdock plant that got stuck to his dog's hair during a walk.⁸ The design of the front portion of Shinkansen bullet train bullet was also inspired by the shape of the kingfisher's beak, to reduce noise and increase engine efficiency.⁹ Also, the connectors of the train were inspired by the silent wings of an owl and the slippery bellies of penguin. Humpback whale fins have inspired the design of efficient wind turbines by decreasing the drag and increasing the lift.^{10,11} Several stunning architectures are also innovated by taking inspiration from nature.^{12,13} For example, the structure of the National Aquatics Center in Beijing developed during 2008 Olympics was inspired by cells and the unique geometry of soap bubbles.^{13,14} Architect Mick Pearce designed the building Eastgate Centre in the capital of Zimbabwe taking inspiration from the mounds of termites.¹⁴ Hence, the need for biomimicry is continuously growing with the advancement of technology and innovation.

Over the years, surface science has become an exciting research area and gained significant attention for various potential applications in daily life, medicine, agriculture, etc. For example, lotus leaf inspired extremely water repellent superhydrophobic surfaces display a great potential for self-cleaning, anti-corrosion, anti-icing, separation of immiscible liquids, etc.¹⁵ Further, inspired by carnivorous nepenthes pitcher plants several industries have developed slippery coatings for different applications such as anti-icing, substance repellence, anti-fouling performance, etc.¹⁶ The following sections discuss liquid-repellent surfaces, focusing on superhydrophobicity and slippery surfaces.

1.2 Natural Examples of Liquid-Repellent Surfaces

Nature is full of wonders enriched with unique features and properties. Wettability is one of the captivating aspects found in nature, with several living organisms having distinctive surface chemistry and wetting characteristics.¹⁵⁻¹⁸ The following section discusses some naturally existing liquid-repellent heterogeneous and homogeneous surfaces i.e., superhydrophobic and slippery surfaces.

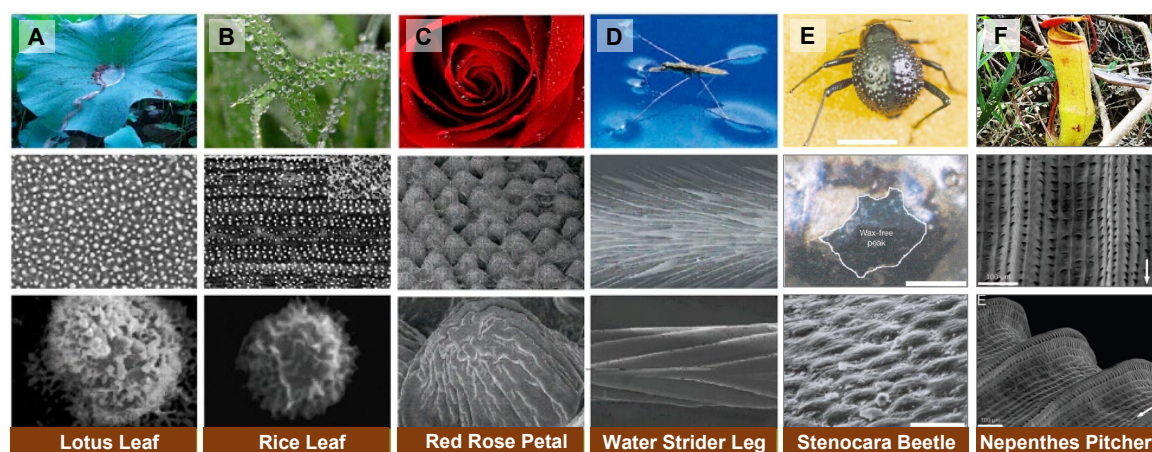


Figure 1.1 Some typical examples of naturally existing liquid repellent surfaces. A-F) Photographs and scanning electron microscope images of non-adhesive superhydrophobic lotus leaf (A), rice leaf possessing anisotropic wettability (B), adhesive superhydrophobic red rose petal surface (C), water repellent water strider leg (D), elytra of stenocara beetle exhibit patterned wettability (E), (Reproduced from Ref. 16 with permission from ACS, copyright 2015), slippery Nepenthes pitcher plant and scanning. Reproduced from Ref. 32 with permission from National Academy of Sciences, Copyright 2004.

Lotus Leaf

Lotus leaf is a well-known example of natural wettability (Figure. 1.1A). It exhibits non-adhesive superhydrophobicity and water droplets can easily roll off from the surface known as lotus effect.¹⁹ During this process, water droplets tend to carry away any deposited dust particles thereby keeping the surface clean. The lotus leaf is often considered as a symbol of purity in many cultures, attributed to its self-cleaning ability. In 1997, Barthlott and Neihuis examined the lotus leaf surface and discovered the existence of rough morphology with micro (10 μm) and nano (100 nm) topography.^{20,21} This rough structure, commonly referred to as a hierarchal micro/nanostructured surface, is coated with hydrophobic epicuticular wax secreted by the leaf itself. The combination of roughness and wax coating contributes to the water-repellent characteristics of lotus leaf. Inspired by the lotus leaf, many artificial superhydrophobic interfaces have been developed for various potential applications including separation of immiscible liquids, anti-fouling, water harvesting, drug delivery, self-cleaning, etc.¹⁷

Rose Petal

Petals of red roses also display superhydrophobicity but with high adhesion (Figure. 1.1C). Water droplets mostly stick to the surface while maintaining the spherical shape and do not roll off from the surface even when the surface is upside down. It is known as ‘petal effect’.²² Feng et al. did a detailed investigation to understand the surface morphology of red rose petals. Scanning electron microscope images revealed the presence of a close periodic array of micropapillae with a 16 μm diameter and 7 μm height.²² Each of these micropapillae consisted of nanometer-sized cuticular folds. Hence, like lotus leaf, rose petal also possess hierarchal roughness and it endows the surface with superhydrophobicity. However, the structural difference in microstructure between these two surfaces contributed to the difference in the adhesive force of beaded water droplets. Due to the larger size of both micro and nanostructures, water droplets can penetrate the micro-grooves but are unable to enter the nanostructures. This impregnation of water to the microgrooves results sticking of water droplets on the rose petal surface.

Rice Leaf

Lotus leaf displays isotropic super-wettability, allowing water droplets to roll freely in all directions. In contrast, rice leaf exhibits anisotropic superhydrophobicity, where the motion of water droplets depends on the direction of micropapillae on the leaf surface (Figure. 1.1B).¹⁹ Although rice leaf contains a similar type of micro/nanostructures as that of lotus leaf, the difference in the arrangements of micropapillae alters the wettability characteristics. Papillae are arranged in two ways — one-dimensional parallel alignment of papillae to the leaf edge and random distributions of papillae in the perpendicular direction to the leaf edge. Water droplets can effortlessly roll along the direction of the leaf edge with minimal surface tilting, whereas significant tilting is required for water droplets rolling along the other direction (perpendicular direction). The different energy barriers arising due to different arrangements of micropapillae contribute to the development of anisotropic superwettability. These findings contributed significantly to the development of controllable and patterned wettability on solid surfaces.^{23,24}

Water Strider Leg

Superhydrophobicity is also a common phenomenon in animals as well. For example, water striders are well known for their ability to walk freely on water surfaces of ponds, slow streams, etc.²⁵ Superhydrophobic legs of water striders help them to stand effortlessly and move around

on the water surface because of the surface tension effect of secreted wax (Figure. 1.1D).^{26,27} The leg does not penetrate the water surface until the formation of a depth of approximately 4 mm. The supporting force of just one leg is enough to support 15 times the total body weight of the insect and the volume of ejected water is almost 300 times that of the leg, indicating its excellent water repellence. Scanning electron microscope analysis of water strider legs revealed the presence of large numbers of oriented needle-shaped tiny hairs (microsetae) with diameters ranging from 3 μm to several hundred nanometres. Further, each microsetae consists of nanoscale grooves, forming a unique hierarchical structure. These structured legs can trap large amounts of metastable trapped air, imparting robust superhydrophobic property. This finding opens an avenue for designing miniaturized aquatic devices.²⁸

Stenocara Beetle

Stenocara beetle, also known as Namib beetle, inhabits the Namib desert in South Africa. Namib desert is one of the most arid regions in the world and this insect developed a remarkable water collection ability to survive in this harsh condition. The beetle has an extraordinary ability to collect water on their back from fog-laden wind that frequently occurs in the Namib Desert (Fig. 1.1E).²⁹ In 2001, Parker et al. discovered the mechanism lying behind this unique water collection ability.³⁰ The beetle usually tilts its body forward, facing the wind to capture water and subsequently, the collected water rolls down to the mouth of the beetle from its top wings. Scanning electron microscopic study of Stenocara beetle elytra revealed the presence of randomly arranged hydrophilic bumps of diameter 0.5 mm with 0.5-1.5 mm distance apart and superhydrophobic valleys. The peaks of these hydrophilic bumps are smooth with no covering. Whereas, hydrophobic valleys along with sloping sides are covered with wax-coated microstructures. These microstructures are composed of flattened hemispheres of 10 μm diameter and organized in hexagonal arrays. The water collection system involves the growth of droplets on the hydrophilic bumps followed by the shedding of growing water droplets. The water droplet first settles on hydrophilic bumps forming fast-growing droplets. Additionally, when water droplets strike hydrophobic regions, it either bounce back or blown away towards the hydrophilic area. After reaching a threshold point, where the size of accumulated water droplets exceeds the contact area of hydrophilic bumps, water droplets detach easily and roll down the tilted hydrophilic valley to the beetle's mouth. Inspired by this unique wettability gradient, different artificial surfaces with patterned wettability have been developed for fog harvesting applications.³

Nepenthes Pitcher Plant

The carnivorous nepenthes pitcher plants are well-recognized for their evolution into organs with a remarkable ability to capture and digest arthropods. These plants generally grow in nutrient-poor environments and digest prey to get nitrogen for their survival.³² Insects are attracted towards these plants due to their fragrance, extrafloral nectar or UV light absorption pattern. When insects sit on the peristome of the plant, they fall into the traps due to the slippery property of the peristome from where it is difficult to escape and are digested by the enzyme present in the pitcher fluid.^{32,33} Detailed investigation of the peristome surface revealed the presence of microscopic cavities between overlapping epidermal cells towards the outside direction of the pitcher plant. In wet conditions, this microstructure traps water or nectar films and exhibits slippery behaviour by inhibiting the interaction between hydrophobic insect feet and peristome surface. Taking inspiration from the nepenthes pitcher plant, artificial lubricant-infused slippery surfaces have been developed for various practical applications.^{16,34}

1.3 Wettability of Solid Surface

Wettability refers to the ability of liquid droplets to remain in contact with solid surfaces.^{35,36} The spreading of a liquid droplet and its shape mainly depends on the balance between two types of forces i.e., the adhesive force of unlike molecules such as between liquid and solid molecules and cohesive force of similar molecules such as between liquid molecules. Wetting of a solid surface is generally characterized by contact angle measurement, which can be defined as the tangential angle of contact made by the liquid droplet on the solid surface at the triple-phase contact point (Fig. 1.2A). Contact angles (θ) are generally categorized as static

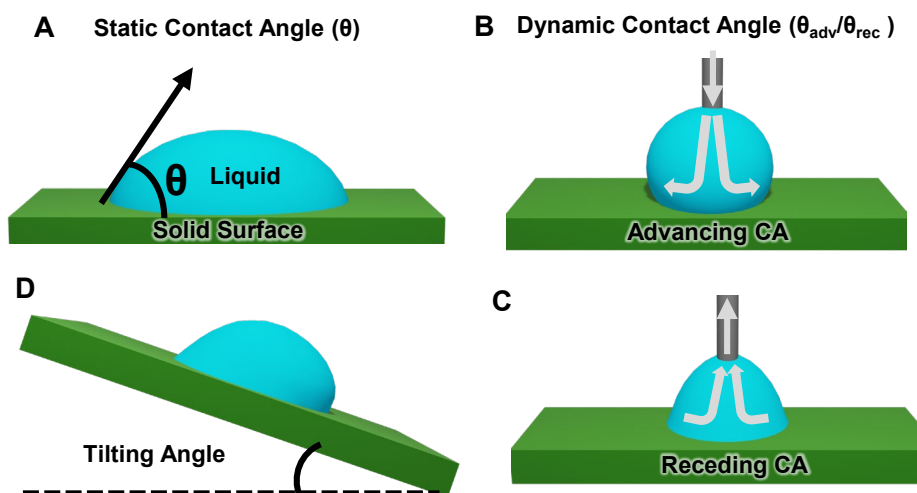


Figure 1.2 Schematic representation of static contact angle (A), advancing contact angle (B), receding contact angle (C), and tilting angle (D).

contact angle and dynamic contact angle. Static contact angle is the equilibrium contact angle made by a liquid droplet on a solid surface, where the solid-liquid contact area remains unchanged during the measurement. Dynamic contact angle refers to contact angles between a liquid droplet and a solid surface, where the three-phase contact line remains in motion with respect to the surface. There are two types of dynamic contact angle — advancing contact angle and receding contact angle.^{37,38} The advancing contact angle on super-liquid repellent surfaces is measured when liquid droplet volume continuously increases (Fig. 1.2B). Whereas, the receding contact angle is measured in the opposite way, when the liquid is withdrawn from the surface and the droplet volume decreases (Fig. 1.2C). The difference between advancing and receding contact angle is known as contact angle hysteresis (CAH).^{39,40,41} Further, the tilting angle refers to the inclined angle of the surface at which the liquid droplets start to slide by gravitational force (Fig. 1.2D).³⁸ Based on contact angle values of water droplets, solid surfaces have been classified into four categories (Fig. 1.3) — a) superhydrophilic surface ($0^\circ \leq \theta \leq 10^\circ$), b) hydrophilic surface ($10^\circ < \theta < 90^\circ$), c) hydrophobic surface ($90^\circ < \theta < 150^\circ$) and d) superhydrophobic surface ($\theta \geq 150^\circ$).⁴² Depending on the contact angle hysteresis value, superhydrophobic surfaces can be further classified as adhesive (CAH $> 10^\circ$) and non-adhesive (CAH $< 10^\circ$) superhydrophobic surfaces.

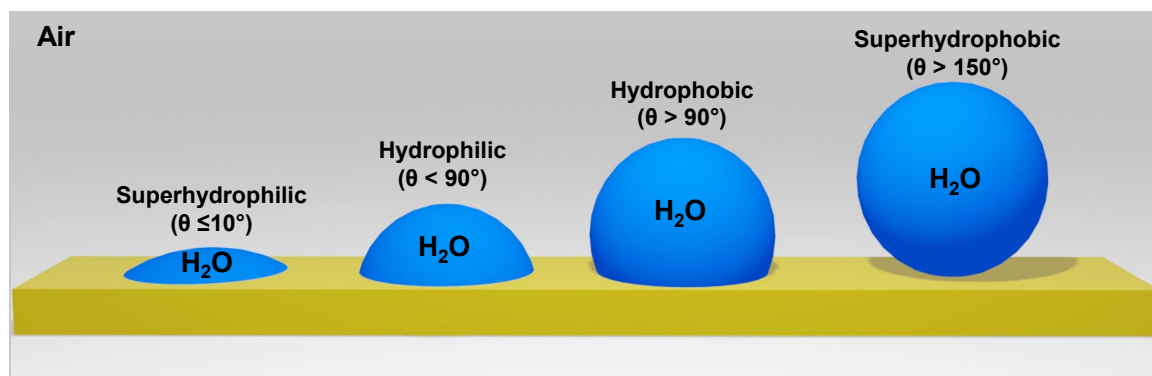


Figure 1.3 Classification of solid surfaces in four categories including superhydrophilic, hydrophilic, hydrophobic and superhydrophobic surfaces based on the static contact angle values of beaded water droplets.

1.4 Theoretical Models of Liquid Repellent Interfaces

1.4.1 Wettability of Solid Surface in Air

Liquid repellence of a solid surface is an important property for manipulating the droplet of liquid on solid surface. Over time, different theoretical models have been introduced to understand the wetting phenomenon of solid surfaces.⁴³ A brief discussion of these wettability theories is included in this section.

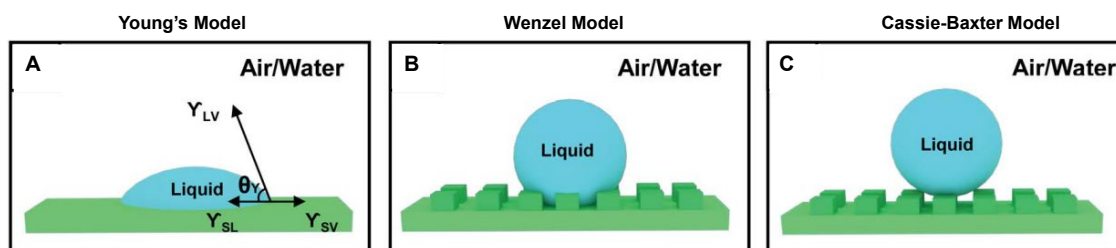


Figure 1.4 Schematic representation of different wettability models on solid surfaces in air A) Young's model, B) Wenzel model and C) Cassie-Baxter model. Reproduced from Ref. 43 with permission from The Royal Society of Chemistry, copyright 2021.

1.4.1.1 Young's Model

In 1805, Thomas Young proposed a model to explain the wetting of homogeneous, smooth ideal solid surfaces (Fig. 1.4A).⁴⁴ When a liquid droplet is placed on ideal solid surfaces, a contact angle (θ_Y) is formed at the interface and it depends on the surface tension of liquid (γ_{LV}), surface free energy (γ_{SV}), and interfacial tension (γ_{SL}). At the equilibrium condition, Young's equation (1.1) can be expressed as follows,

$$\cos\theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \dots\dots\dots(1.1)$$

This equation is justified as the result of thermodynamic equilibrium at the three-phase interface (solid-liquid-vapour) formed by the liquid droplet on the solid surface.

1.4.1.2 Wenzel Model

Young's equation is only applicable for ideally smooth homogeneous solid surfaces. However, surfaces typically possess a certain amount of roughness. In the case of chemically homogeneous but rough surfaces, the actual surface area is greater than the apparent surface area by a factor r , known as the roughness factor introduced by Wenzel in 1936 (Fig. 1.4B).⁴⁵ Wenzel modified Young's model by incorporating this roughness factor into the equation. According to the Wenzel model, liquid fills the rough structures of the solid surface and consequently, both interfacial tension of solid-liquid and solid-vapour should be multiplied by the roughness factor. The minimum thermodynamic energy state results in the following Wenzel equation (1.2)

$$r\gamma_{SV} = r\gamma_{SL} + \gamma_{LV}\cos\theta_W$$

$$\cos\theta_W = \frac{r(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} \dots\dots\dots(1.2)$$

Where θ_w is the apparent Wenzel contact angle of the solid surface. Considering equation (1) and equation (2), established the following relationship between θ_Y and θ_w

$$\cos\theta_w = r\cos\theta_Y$$

Since $r \geq 1$ for rough surfaces, the presence of surface roughness enhances the wetting and non-wetting characteristics of a solid surface depending on the nature of its intrinsic wettability. For example, smooth surfaces with $\theta_Y < 90^\circ$, association of roughness make the surface more hydrophilic. Whereas hydrophobic smooth surfaces with $\theta_Y > 90^\circ$ become more hydrophobic when associated with roughness.

1.4.1.3 Cassie and Baxter Model

Wenzel model is valid for rough solid homogeneous surfaces where liquid remains in complete contact with solid surfaces. However, this model fails to explain the wetting behaviour of solid surfaces with exceptionally large values of roughness factor ($r \gg 1$). To overcome this limitation, another wettability model was proposed by Cassie-Baxter in 1944 by considering the surface chemistry (Fig. 1.4C).⁴⁶ According to this model, liquid remains suspended on the top of the asperities of the microporous structures due to the presence of the metastable trapped air layer within the grooves. Thus, the apparent solid-liquid contact area is composed of two different interfaces i.e., solid-liquid interface and liquid-vapor interface, which is considered as heterogeneous wetting of the solid surface. According to this model, the apparent contact angle is described as

$$\cos \theta_{CB} = f_1 \cos \theta_1 + f_2 \cos \theta_2 \dots\dots\dots (1.3)$$

$$f_1 + f_2 = 1$$

Where f_1 and f_2 are the fraction of contact area solid-liquid and liquid-vapor interface, respectively. θ_1 and θ_2 refer to the contact angle of liquid droplet on a flat solid surface ($\theta_1 = \theta_Y$) and air. The contact angle (θ_2) of a liquid droplet in the air is 180° , then the above equation can be rewritten as

$$\cos \theta_{CB} = f_1 \cos \theta_Y + (1-f_1) \cos (180^\circ)$$

$$\cos \theta_{CB} = f_1 (1 + \cos \theta_Y) - 1$$

This equation is only valid for contact angle measurements for rough surfaces without any liquid penetration in the grooves.

Additionally, in some instances, surfaces also exhibit a mixed wetting state in which liquids partially penetrate and wet the asperities while partially remaining suspended on the trapped air layer. This is generally identified as the transition of wetting from Wenzel state to Cassie-Baxter state^{47,48} and the apparent contact angle has been defined as follows

$$\cos \theta_{mix} = rf_1 \cos \theta_Y + f_1 - 1$$

Where r is the roughness factor of the solid surface.

1.4.2 Wettability of Liquid Infused Solid Surface

The previous section includes a discussion about the hydrophilic/ hydrophobic wettability of solid surfaces in air. However, low surface tension liquids such as organic solvents and oils can readily wet superhydrophobic interfaces by penetrating the micro-nano grooves of the rough solid surface. To avoid fouling of solid surfaces by both oil and water, often a complex topography with re-entrant surface curvature and fluorinated chemical modification is adopted.⁴⁹⁻⁵² Developing such complex topography on a large scale maintaining high durability is difficult. Recently, lubricant infused slippery surfaces have emerged as a promising alternative that prevents fouling of solid surfaces by readily sliding droplets of a wide range of liquids having differences in surface tensions. Taking inspiration from the slippery behaviour of *Nepenthes pitcher plant*, in 2011 Wong et al. developed an omniphobic slippery liquid-infused porous surface by infusing a fluorinated lubricant Perfluorotripentylamine (FC70) into

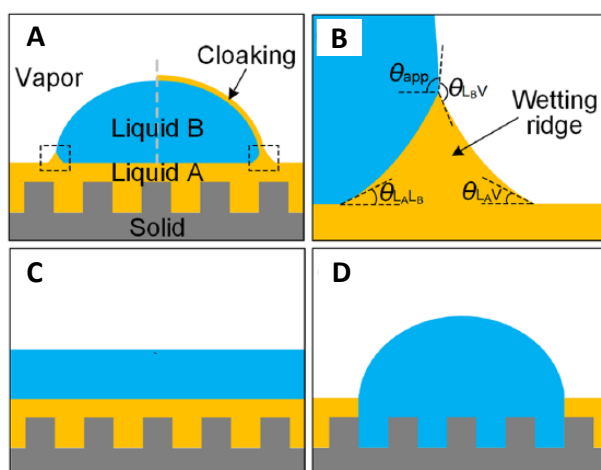


Figure 1.5 Different wetting modes of solid surface infused with liquid A. A) Schematic representing the anchoring of stable liquid B droplet. The left part shows the liquid B droplet not being cloaked, and the right part shows the cloaking of the liquid B droplet with the infused liquid A. The dashed box shows the ridged portion of the cloaked droplet. B) Schematic representation of zoomed in image of ridged portion. C) Schematic of spreading of liquid B on the infused liquid. D) Schematic depicting the penetration replacement of infused liquid layer and penetration of liquid B droplet forming a new solid-liquid interface. Reproduced from Ref. 57 with permission from The Royal Society of Chemistry, copyright 2022.

Teflon nanofibrous membrane.⁵³ The omniphobic fluorinated lubricant readily spreads and wets the porous surface through capillary wicking, forming a layer atop the porous structure that remains mostly immiscible and repellent towards aqueous and organic solvents. The wetting of a liquid-infused solid surface is significantly different from the surface directly exposed to air. When a solid surface is infused with a liquid phase (liquid A, L_A), it forms a thin layer on top of the solid surface. Subsequently, the wetting of such surface towards another immiscible liquid (liquid B, L_B) depends on interfacial tension of four different phases i.e., solid– liquid A (γ_{SL_A}), liquid A–vapor (γ_{L_AV}), liquid A–liquid B ($\gamma_{L_AL_B}$) and liquid B–vapor (γ_{L_BV}). Interfacial tensions of these four different phases significantly impact the stability of liquid infused slippery surfaces⁵⁴⁻⁵⁷ and create different wettability conditions —

$$\gamma_{SV} - (\gamma_{LV_A} + \gamma_{LV_B}) > 0 \dots\dots\dots(1.4)$$

$$\gamma_{L_BV} - (\gamma_{L_AL_B} + \gamma_{L_AV}) > 0 \dots\dots\dots(1.5)$$

$$\gamma_{L_AV} - (\gamma_{L_AL_B} + \gamma_{L_BV}) \geq 0 \dots\dots\dots(1.6)$$

$$\gamma_{SV} - (\gamma_{SL_A} + \gamma_{L_AV}) \leq -\frac{r-1}{r-f_1} \gamma_{L_AL_B} \dots\dots\dots(1.7)$$

Under the condition (1.4), introducing liquid B to the surface cannot displace the infused liquid phase (L_A) from the surface and forms a discrete droplet on the surface (Figure 1.5A). Whereas under the situation (1.5), infused liquid phase cover liquid B and forms a layer around the droplet of liquid B. This situation is known as clocking (Figure 1.5A). In another condition (1.6), liquid B completely displace the infused liquid phase (L_A) and forms a uniform layer instead of droplet formation (Figure 1.5C). However, under condition (1.7), the third liquid phase (L_B) displace the infused liquid (L_A) only from the contact area and forms a new solid-liquid (L_B) interface (Figure 1.5D). Here, r and f_1 correspond to roughness factor and fraction of solid-liquid contact area, respectively.

1.5 Essential Criteria to Design Liquid Repellent Interfaces

Lotus leaf is a well-known example of a naturally existing non-adhesive superhydrophobic surface with water static contact angle $\sim 160^\circ$ and contact angle hysteresis $\sim 2^\circ$.^{19,58-60} Detailed investigation of the lotus leaf surface reveals the presence of micro-nano structures coated with epicuticular wax. The high water contact angle is due to the combination of both hierarchal rough structures and wax coating. The rough morphology provides enough space to trap metastable air layer in the microgrooves and wax provides low surface free energy. From the

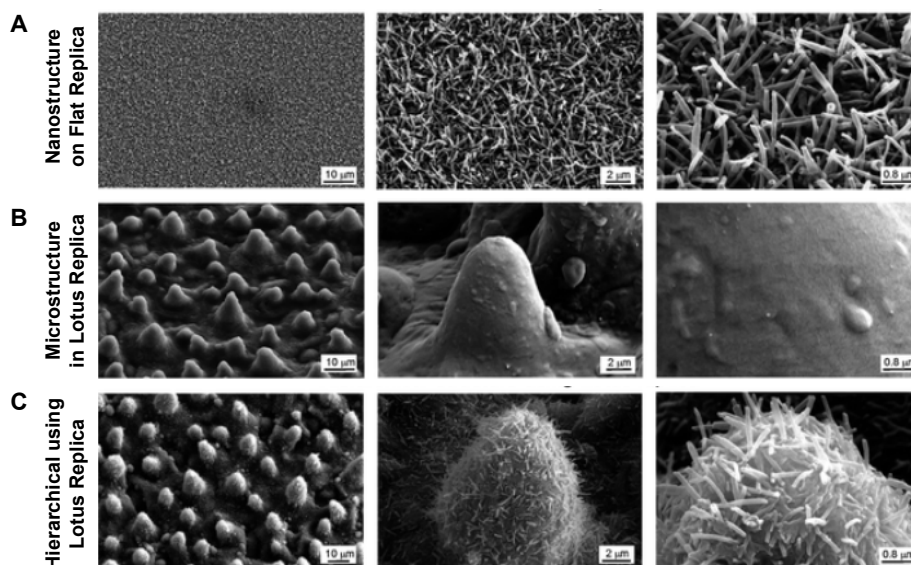


Figure 1.6 Scanning electron microscope images of nanostructured surface on flat replica (A), microstructured surface on lotus replica (B) and micro/nanostructured hierarchical surface (C) on lotus replica. Reproduced from Ref. 59 with permission from The Royal Society of Chemistry, copyright 2009.

numerical study it was observed that only micro-structured surface coated with wax can reach water contact only up to 147° , which is much smaller compare to experimentally measured value, due to the rapid displacement of trapped air from microgrooves. Further, only the nanostructured interface is incapable to trap enough metastable trapped air required for attaining superhydrophobicity. Hence, rough surface (micro-nano topography) with low surface energy coating is required for attaining superhydrophobicity like lotus leaf.⁵⁹ In summary, there are two essential criteria needs to be satisfied during the development of artificial superhydrophobic surfaces-a) rough surface with micro-nano topography and b) low surface free energy.

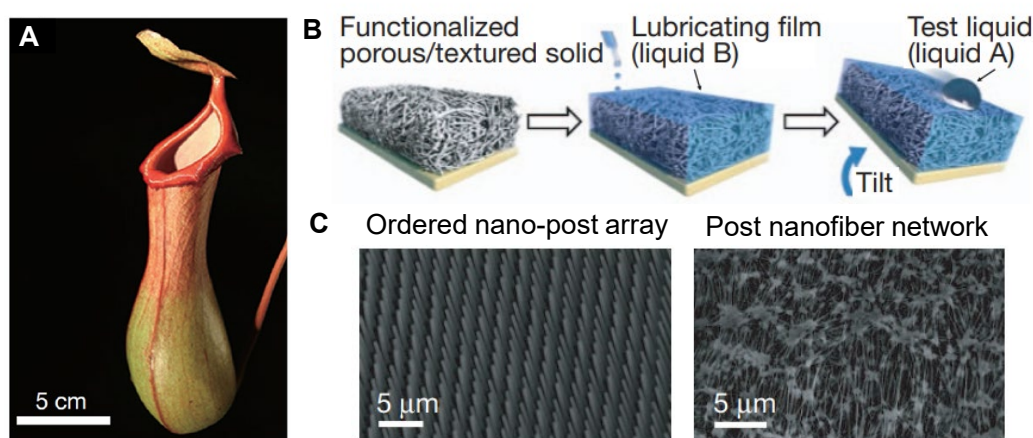


Figure 1.7 A) Photographs of *Nepenthes* pitcher plant. B) Schematic representing the fabrication of a slippery surface by infusing low surface energy, chemically inert lubricant into a porous/textured surface to form a chemically homogeneous and smooth surface. C) Scanning electron microscope images of porous/textured surfaces. Reproduced from Ref. 53 with permission from Springer Nature Limited Copyright 2011.

Slippery surfaces generally involves simple design compare to superhydrophobic surface. Inspired by *Nepenthes* pitcher plant, lubricant infused slippery surfaces are mostly developed by infusing lubricant to a rough hydrophobic or superhydrophobic porous surface, resulting in a smooth surface (Fig. 1.7).^{34,53,61,62} However, some essential criteria needs to be satisfied for developing stable lubricant infused slippery interface. Aizenberg and co-workers first proposed three standard criteria for designing artificial slippery surfaces and those are as following—

- i) The textured surface must be readily wet by the lubricant and lubricant must strongly adhere to the surface.
- ii) Surface should have preferential wetting by the lubricant compare to the repellent liquid.
- iii) Lubricant layer should be immiscible and incompatible with the liquid to be repelled.

1.6 Applications of Superhydrophobic and Slippery Surfaces

Over the years, the development of different liquid-repellent interfaces has gained enormous attention due to its wide range of applications in different directions such as oil-water separation, anti-fouling, anti-icing, drug delivery, water harvesting, energy harvesting, anti-corrosion, etc.^{56,57} Some conventional applications of artificial superhydrophobic and slippery surfaces are discussed in this section as follows:

1.6.1 Oil-Water Separation

Contamination of water with oils due to oil spillage accidents, and discharge of industrial waste pose a serious threat to the environment and human health.⁶³⁻⁶⁶ Several efforts are being made to address this problem, such as in situ burning, mechanical devices, bioremediation, catalytic decomposition, separation of immiscible liquids, etc.⁶⁷⁻⁶⁹ Notably, the simple physical separation process gained huge attention due to its ability to simultaneous separation and easy collection of both liquids. The use of superhydrophobic interfaces to separate oil-water mixtures is found to be an effective approach following the physical separation method.⁶⁹⁻⁷⁵ In 2004, Feng et al. first reported a coated a metal mesh displaying both superhydrophobic and superoleophilic property for effective separation of immiscible oil-water mixture. Spray deposition of low surface energy polytetrafluoroethylene (PTFE) emulsion created a crater-like rough morphology on the stainless steel surface without blocking the open pores of the mesh.⁷⁰ This coated metal mesh displayed non-adhesive superhydrophobicity with water contact angle $> 150^\circ$ and roll-off angle 4° . In contrast, diesel oil droplet readily spread and permeate through the membrane within 240 ms. The coated mesh exhibiting both

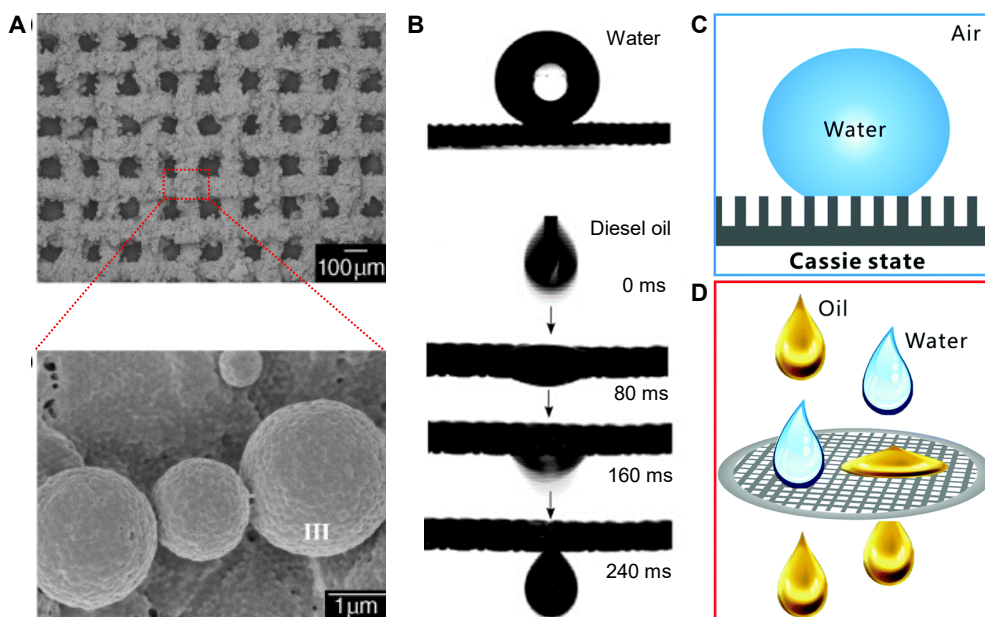


Figure 1.8 A) Scanning electron microscope images of coated stainless steel mesh. B-D) Photographs (B) and schematic (C, D) showing the water repellence and spreading and permeating behaviour of diesel oil from the coated superhydrophobic mesh. Reproduced from Ref. 70 with permission from WILEY-VCH Verlag GmbH & Co. KGaA Weinheim, Copyright 2004. Reproduced from Ref. 71 with permission from The Royal Society of Chemistry, copyright 2018.

superhydrophobicity and superoleophilicity was further utilized for effective separation of water-diesel oil mixture with 95% separation efficiency (Figure 1.8). In a separate report, Ruidas et al. prepared a covalent organic framework (COF) using two monomers 2-hydroxy-1,3,5-benzenetricarbaldehyde and 2,4,6-tris(4-aminophenyl)-1,3,5-triamine and subsequently coated with long hydrocarbon chain modified silane moiety to impart superhydrophobicity.⁷² The resulting superhydrophobic COF effectively separated oil/oily components from oil/water mixture with high absorption efficiency (above 1000 wt%). Such membrane however remained incapable in separating oil-in-water emulsion. Cheng et al. reported the fabrication of a superhydrophobic membrane by integrating polyvinylidene fluoride and polydimethylsiloxane-based solutions following a simple electrospinning approach.⁷³ They have further demonstrated the successful separation of water-in-oil emulsions utilizing this membrane with a separation efficiency of more than 99.6%.

Mostly superhydrophobic interfaces have been predominantly investigated for separating mixtures of immiscible liquids and as slippery surfaces can repel both water and oils, it has not been explored widely for such applications. However, recently slippery surfaces have also been explored for separating immiscible oil-water mixture.⁷⁶⁻⁷⁹ Wang et al. designed a superamphiphilic porous membrane and regulated its wettability lubricants with high polar surface energy, resulting the membrane to repel low surface energy immiscible liquids. Utilizing this repellence

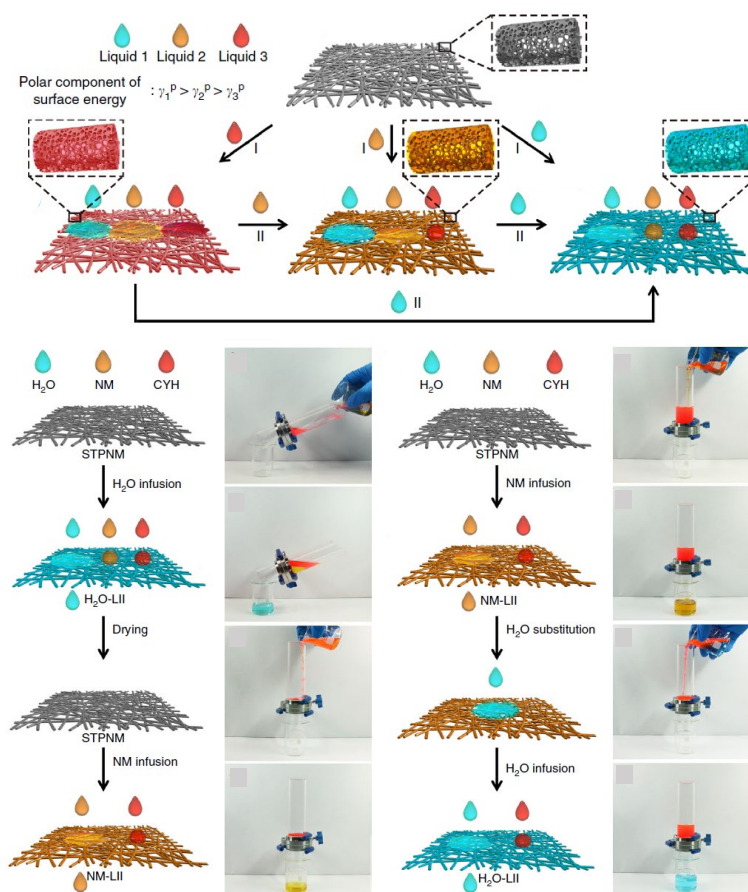


Figure 1.9 Schematic and photographs representing the separation of a multiphase liquid mixture composed of water, cyclohexane, and nitromethane through the strategic infusion of water and nitromethane into the porous membrane. Reproduced from Ref. 76 with permission from Springer Nature Limited Copyright 2017.

concept, the lubricant-infused membrane was used to separate mixtures of different immiscible liquids even with minimal difference in surface energy as low as 2 mJm^{-2} (Fig. 1.9).⁷⁶

1.6.2 Water Harvesting

Inspired by Namib desert beetle, and spider silks, harvesting water from fog or atmosphere is emerging as a promising and sustainable alternative source of fresh water.^{24,79-82} Liquid-repellent superhydrophobic and slippery surfaces have been used extensively in designing efficient water collection systems where superhydrophobicity and slippery background combined for efficient shedding of water droplets.⁸³⁻⁸⁸ Guo et al. reported a superhydrophilic-superhydrophobic patterned surface and compared its fog harvesting efficiency with surfaces having single wettability.⁸³ The venation-like patterned surface remained effective in harvesting water with a 225.6% water collection rate (Fig. 1.10A-C). In another report, Li et al. developed a superhydrophobic-superhydrophilic patterned aluminium surface with a combination of laser and chemical treatment.⁸⁴ This patterned surface exhibited excellent water harvesting efficiency and achieved a water harvesting rate of $0.85 \text{ kg m}^{-2} \text{ h}^{-1}$.

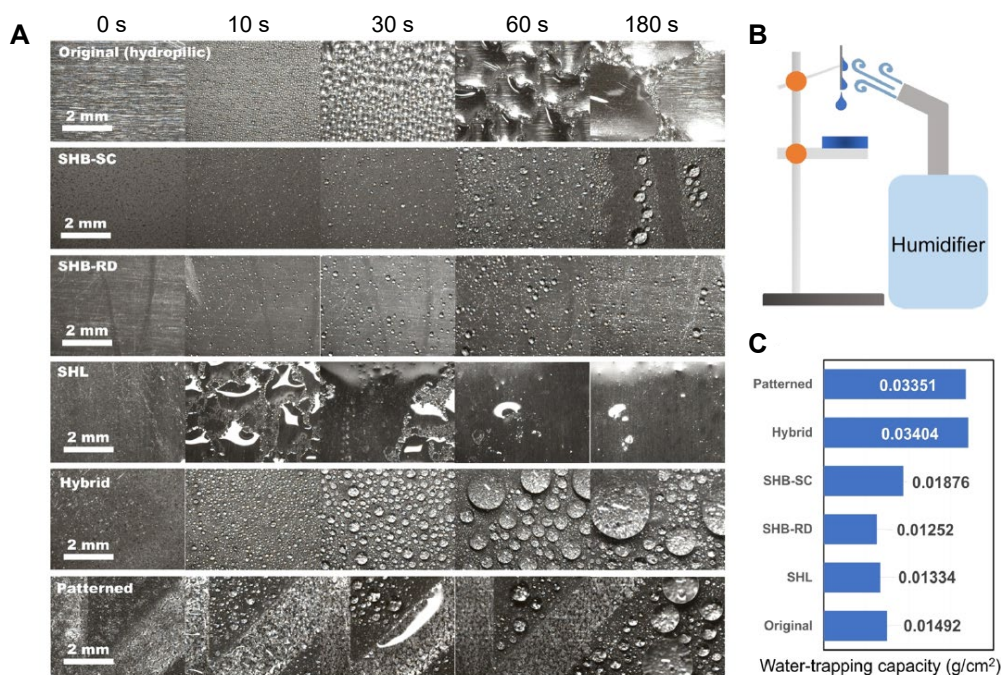


Figure. 1.10 A) Photographs showing the progress of water harvesting on the surfaces with different wettabilities— original hydrophilic zinc plate, superhydrophobic surfaces obtained via spray coating (SHB-SC) and replacement deposition (SHB-RD), superhydrophilic, hybrid and patterned surface. B) Schematic representation of water collection system. C) Graph comparing the water trapping capacity of surfaces with different wettabilities. Reproduced from Ref. 83 with permission from American Chemical Society, copyright 2012.

While superhydrophobic surfaces have been used extensively for water harvesting applications, a major challenge arises due to the displacement of metastable trapped air phase from the grooves of the superhydrophobic surfaces during prolonged exposure to humid conditions. This displacement of the air phase compromises the water repellence of the superhydrophobic surfaces and delays the fluidity of condensed water droplets. To address this issue, slippery surfaces with long-term stability in humid environments have emerged as an alternative approach for collecting water from the atmosphere.⁵⁶ Feng et al. studied the water harvesting efficiency of a stable slippery surface developed through infusing silicon oil into a micro/nanostructured surface. The combination of both micro and nanostructures in the porous network inhibited the loss of lubricant and displayed an excellent water collection efficiency as high as $852 \text{ mg cm}^{-2} \text{ h}^{-1}$ (Figure 1.11).⁸⁷ Park et al. reported a conceptually different design by combining the principles of Namib desert beetles, cacti and pitcher plants for water droplet condensation and compared its performance with other synthetic surfaces.⁸⁸ Faster condensation and growth of water droplet was achieved by designing optimal topography based on the radius of curvature and cross-sectional shape with the integration slippery nanocoating inspired by nepenthes pitcher plant. This surface displayed high water collection efficiency compared to other surfaces.

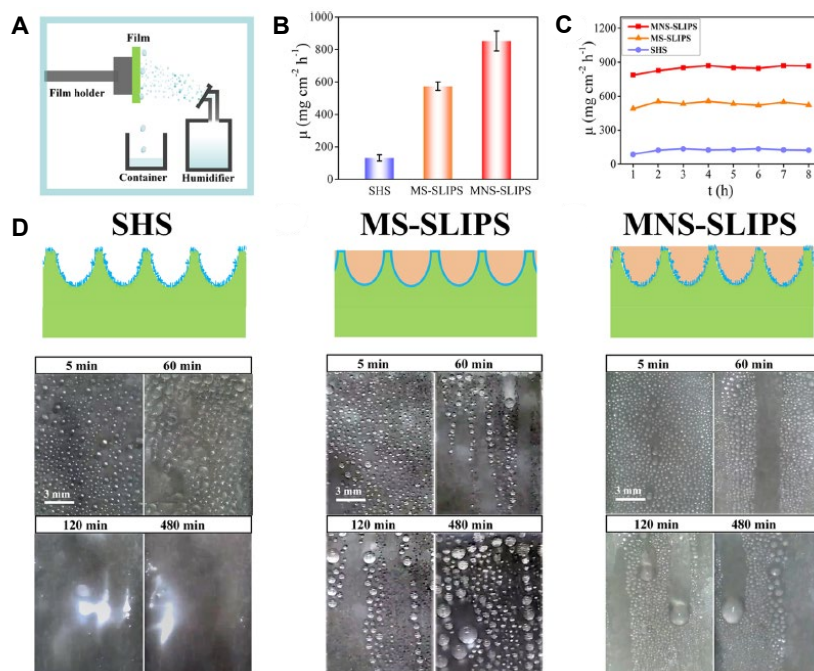


Figure 1.11 A) Schematic representation of fog harvesting set up. B,C) Graph showing the comparison of water collection rate and water collection performance of superhydrophobic (SHS), microstructured slippery (MS-SLIPS) and micro/nanostructured slippery (MNS-SLIPS) surface. D) Photographs comparing the capture, coalescence and collection of fog on SHS, MS-SLIPS and MNS-SLIPS surface for 8 h. Reproduced from Ref. 87 with permission from American Chemical Society, copyright 2012.

1.6.3 Anti-fouling

Bio-fouling i.e., adherence and unwanted accumulation of bio-organisms such as biofilm growth, platelet adhesion, etc on surfaces including medical devices, marine infrastructures, water pipes and food packaging is a widespread problem.⁹⁰⁻⁹² Liquid-repellent superhydrophobic and slippery coatings mostly act as a protective layer and restrict the contamination of underlying substrates with such bio-organisms.^{93,94} This anti-fouling performance makes such surfaces suitable for potential applications related to bio-medical devices, marine industries, etc.⁹⁴ Wen et al. reported the fabrication of flame retardant superhydrophobic paper with specified layered network structures following a facile green method. The superhydrophobic paper displayed remarkable resistance towards the attachment of *E. coli* and *S. aureus* bacteria on the surface, even after incubating the paper in bacterial solutions for 24 h, separately (Fig. 1.12A, B).⁹⁵ The anti-wetting property of the coated paper restricts bacterial adhesion and zinc oxide particles present on the coating contributed to killing the bacteria. In contrast, substantial growth of the bacterial colony was visible on raw paper, indicating its inability to showcase anti-bacterial activity. In addition to superhydrophobic materials, slippery surfaces also exhibited excellent anti-fouling performance due to indirect contact between bio-organisms and substrate.⁹⁶⁻⁹⁹ Tesler et al. reported a new synthetic route to

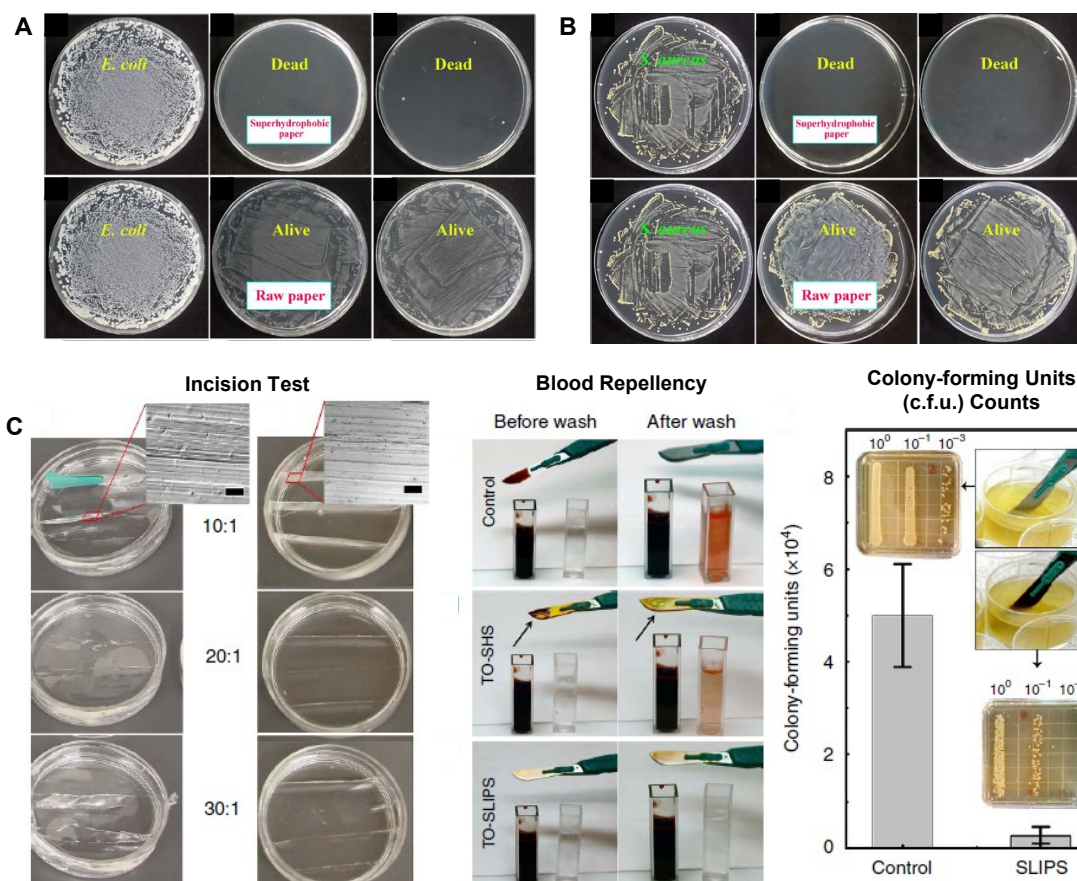


Figure 1.12 A,B) Photographs showing the anti-bacterial performance of raw paper and superhydrophobic paper against *E. coli* (A) and *S. aureus* (B). Reproduced from Ref. 95 with permission from Elsevier B.V., copyright 2018. C) Photographs and c.f.u counts graph representing the anti-fouling performance of TO-SLIPS. Reproduced from Ref. 100 with permission from Macmillan Publishers Limited, part of Springer Nature, copyright 2015.

develop an anti-fouling omniphobic slippery surface by chemical vapour deposition of titanium oxide (TO) nanoparticles on stainless steel.¹⁰⁰ The nanoparticle deposited surface was chemically modified with low surface free energy perfluoroalkyl-bearing phosphate molecule resulting TO-loaded superhydrophobic surface, referred as TO-SHS and further infused with perfluoropolyether lubricants to obtain omniphobic TO-loaded slippery surfaces, denoted as TO-SLIPS. TO-SLIPS effectively prevented the adhesion of blood and retained its slippery property even after submerging the surface in a cuvette filled with blood. Whereas, TO-SHS completely lost its anti-wetting property upon immersion in blood, leading to blood adherence on this superhydrophobic surface (Fig. 1.12C). Additionally, the slippery surface also restricted the growth of bacteria and algae, suggesting its potential use in marine applications.

1.6.4 Anti-icing

Preventing surfaces from ice accumulation and freezing is necessary for ensuring the unperturbed operation of many outdoor applications.¹⁰¹ Both superhydrophobic and slippery

coating are considered as promising approaches for anti-icing applications.¹⁰²⁻¹⁰⁵ Wang et al. developed an ice-repellent superhydrophobic surface composed of poly(dimethylsiloxane) (PDMS) and zinc oxide.¹⁰⁶ Hierarchical micro/nano topography of the surface and low surface energy coating with heptadecafluorodecyl tripropoxy silane molecule contributed to anti-icing performance. The non-adhesive water repellence of the surface remained intact even after keeping the coating at -20 °C temperature for 3 months at a relative humidity of 90% (Fig. 1.13A, B). Moreover, the surface displayed an excellent de-icing phenomenon, as the accumulated ice could be removed easily from the surface by just simply vibrating the surface for 30 s.

Additionally, slippery surfaces have also been exploited largely for anti-icing applications.^{107,108} In a study by Kim et al., an ultra-smooth anti-icing slippery coating was reported on a widely used aluminium surface.¹⁰⁸ The coating was developed by electrochemical deposition of polypyrrole on aluminium surface, followed by fluorination and subsequent

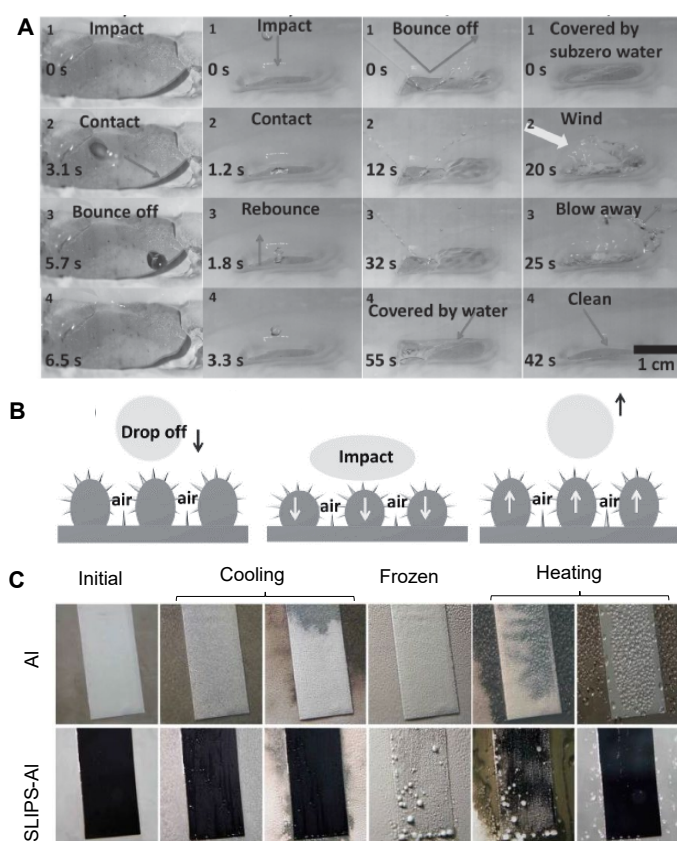


Figure 1.13 A) Photographs depicting the impact test of water droplet and durability of superhydrophobic substrate after keeping the surface at low temperature (-20 °C) and high humidity (90 %) for 3 months. B) Schematic illustration of interfacial analysis of microstructured superhydrophobic surface. Reproduced from Ref. 106 with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2016. C) Photographs showing the ice formation by deep freezing (-10 °C) at high humidity (60 % RH) and de-icing by heating on a bare aluminium surface (Al) and slippery aluminium (SLIPS-Al) surface. Reproduced from Ref. 108 with permission from American Chemical Society, copyright 2012.

lubricant infusion. This surface prevented ice adhesion by repelling condensed water droplets before freezing. Also, the surface displayed an easy removal of accumulated ice by tilting the surface under gravity (Fig. 1.13C).

1.6.5 Anti-corrosion

The liquid-repellent superhydrophobic and slippery coating protects metal surfaces against corrosion in humid or saline environments by minimizing the solid-liquid contact or preventing the direct contact of liquid, respectively.¹⁰⁹⁻¹¹¹ For example, a superhydrophobic coating developed by Li et al. exhibited an outstanding anti-corrosion performance.¹¹² The coating was developed on various substrates by spray depositing a reaction mixture composed of epoxy resin, polydimethylsiloxane, and modified silicon dioxide (SiO₂). Moreover, the coated magnesium (Mg) alloy displayed excellent anti-corrosion performance with 98.9% corrosion inhibition efficiency measured in 3.5 wt% sodium chloride (NaCl) solution. The metastable trapped air layer on the rough surface of the coating minimized the contact between corrosive liquid and solid substrate, inhibiting the corrosion loop formation.

Similarly, the application of slippery coatings has been effective in preventing corrosion on metal surfaces under harsh environments. Zhang et al. prepared a double-layer slippery coating on AZ31 Mg alloy for anti-corrosion application.¹¹³ The slippery coating effectively protected the Mg alloy from corrosion even after 7 days of immersion in 3.5 wt% NaCl solutions.

1.6.6 Other Applications

Apart from the applications discussed above, superhydrophobic and slippery interfaces have many other prospective applications such as drug delivery,^{114,115} energy harvesting,^{116,117} droplet manipulations,¹¹⁸⁻¹²⁰ drag reduction,¹²¹⁻¹²³ etc. Recently, smart patterned interfaces with extremes of water wettability i.e., superhydrophobicity and superhydrophilicity have been investigated for information hiding and demonstrated their potential for anti-counterfeiting application.^{124,125} Moreover, surfaces with contrast of wettability has been explored for wide range of applications such as cell on a chip, energy harvesting, microreactors, microfluidics, etc.¹²⁶⁻¹³²

1.7 Fabrication Methods of Artificial Superhydrophobic and Slippery Surfaces

Due to an enormous number of prospective applications, various design strategies have been developed over the years to fabricate artificial liquid-repellent interfaces focusing on essential criteria discussed in section 1.5. The methods involved in preparing superhydrophobic

interfaces can be classified broadly into two categories, including ‘top-down approach’ and ‘bottom-up approach’.¹³³ The top-down approach involves the generation of roughness in a material through different techniques — lithography, plasma etching, printing, etc. In contrast, bottom-up approach involves the development of rough surfaces by assembling small building blocks following different methods such as spray deposition, dip coating, layer-by-layer deposition, etc.¹³³ Slippery surfaces are mostly developed by infusing lubricants into the textured surface.³³ However, for practical applications, the robustness and durability of these developed interfaces require major attention. Recently different fabrication strategies have been employed to enhance their durability.¹³⁴⁻¹⁴⁷ This section will give a brief overview of the recently developed strategies for designing robust and durable liquid-repellent interfaces.

1.7.1 Optimization of Matrix and Chemistry

The mechanical robustness and durability of liquid repellent materials largely depend on the chemical composition of the underlying substrates. Utilization of hard materials and nanoparticles generally improves the mechanical robustness, while employing chemically inert components enhances the chemical durability of liquid-repellent materials. For example, a commonly used engineering material, concrete, well known for its exceptional mechanical strength and robustness, has been used largely to develop mechanically robust and durable superhydrophobic materials that can tolerate severe physical and chemical abrasions such as sandpaper abrasions, knife scratch test, adhesive tape peeling test, impact test, exposure to acidic and alkaline solutions, etc.¹⁴⁸ Lu et al. designed a strategy to develop a durable superhydrophobic surface using perfluorooctyltriethoxysilane coated titanium dioxide (TiO₂) nanoparticles.¹⁴⁹ The ethanolic suspension of this nanoparticle can be deposited on the substrates through various techniques, including spray deposition, dip coating and paintbrush method. As shown in Fig. 1.14, all organic mechanically robust superhydrophobic coating was prepared with fluorinated epoxy resin and perfluoropolyether, embedded with PTFE nanoparticles.¹⁵⁰ The epoxy resin provides both mechanical and chemical robustness by strongly adhering to the substrates and efficiently dispersing nanoparticles through hydrophilic functional groups. The perfluoropolyether controls the surface energy whereas, the PTFE nanoparticles provide morphology and low surface energy. The coating can survive the water impact test of a 2.5 mm diameter water jet with a speed of $\sim 35 \text{ ms}^{-1}$. All these organic components help to enhance the chemical robustness of the developed coating and the coating displayed a water contact angle $> 150^\circ$ even after exposure to aqua regia for 60 min and 12M aqueous solution of sodium hydroxide (NaOH) for 12 h. In another report, Ma et al. used PTFE

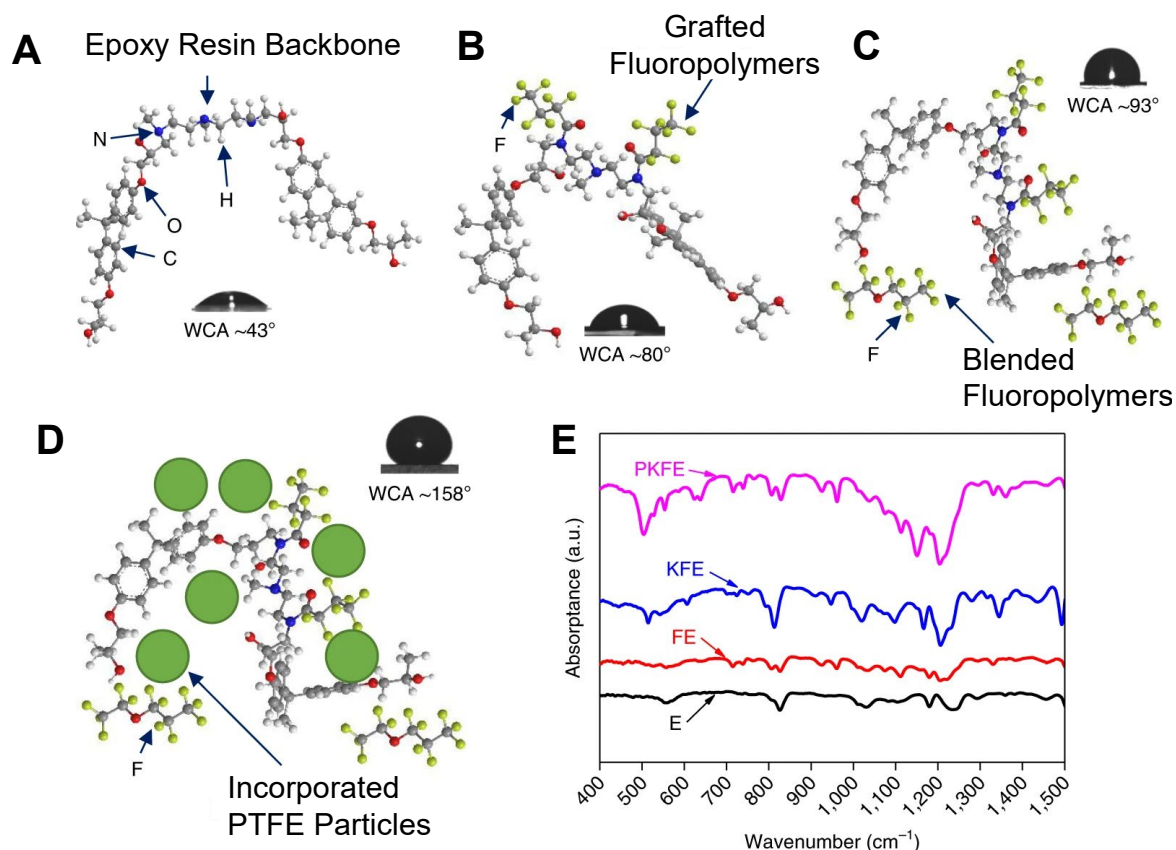


Figure 1.14 A-D) Schematic representing the fluorination strategy to develop robust all-organic superhydrophobic coating and wettability demonstration through contact angle measurement of different chemical components — epoxy resin (denoted as E) backbone (A), fluoropolymer grafted epoxy (denoted as FE) resin (B), blended perfluoropolyether into FE resin (denoted as KFE resin, C) and incorporation of PTFE particles (denoted as PKFE coating, D). E) FTIR spectra of epoxy resin, FE resin, KFE resin and PKFE coating. Reproduced from Ref. 150 with permission from Macmillan Publishers Limited, part of Springer Nature, copyright 2018.

nanoparticles and fluorinated acrylic copolymer to construct a superhydrophobic coating following the spray deposition technique.¹⁵¹ This surface exhibited excellent mechanical robustness and can sustain various physical abrasions such as sandpaper abrasion for 1000 cycles under an applied pressure of 10 kPa, water jet (30 kPa) impact test for 600 min, etc. Also, the presence of PTFE nanoparticles improves the chemical stability of the coating allowing it to withstand exposure to 1.5 mol/L NaOH and 0.75 mol/L H₂SO₄ (sulphuric acid) for 300h, UV (ultraviolet) irradiation tests, and immersion to seawater for 30 days.

Optimization of surface free energy is essential in establishing the liquid repellence of a substrate. Typically, fluorinated thiols, silanes and fatty acids with long hydrocarbon side chains are used to lower the surface free energy of the surfaces to achieve water repellence. Wang et al. fabricated superhydrophobic coatings by modifying stainless steel surfaces with stearic acid and 1H,1H,2H,2H-perfluorodecyltrichlorosilane.¹³⁹ Although both coatings

exhibited comparable water repellence, the fluorinated modified surface showed better chemical resistance towards aqueous solution corrosion. However, due to the adverse side effects of fluorinated compounds, now-a-days non-fluorinated compounds with longer hydrocarbon side chains (e.g., aliphatic amines or thiols with long hydrocarbon chains, wax, PDMS, stearic acid, etc) are being considered as a viable alternative for developing water repellent interfaces.^{152,153} Cao et al. prepared environmentally friendly non-fluorinated robust superhydrophobic fabric by depositing optimized ormosil solution through the dip coating method followed by coating with PDMS.¹⁵⁴ The PDMS layer not only increases the adhesion strength of the coating with the underlying materials but also enhances the micro-roughness of the coating, resulting in a stable superhydrophobic coating.

Additionally, the alteration of surface chemistry represents a strategic approach to enhance the stability of the infused lubricant within the porous network during the fabrication of SLIPS. Typically, oily lubricants readily wet the hydrophobic porous network and stably adhere to the porous structure. Wong et al. prepared two different sets of porous structures including periodically ordered arrays of nanoposts modified with low surface free energy polyfluoroalkyl silane and random network of Teflon nanofibers. After infusing these porous network with low surface tension fluorinated liquid krytox, the infused film displayed repellence towards various liquids surface tension ranging from 72.4 to 17.2 mNm⁻¹ (Fig. 1.7B, C).³³ Liu et al. developed an omniphobic coating by infusing a commercially available fluorinated polytetrafluoroethylene (PTFE) aqueous suspension as a lubricant into porous polytetrafluoroethylene film following spin coating method.¹⁵⁵ This coating exhibited excellent liquid repellence towards different liquids such as water, n-decane, ethanol and crude oil with sliding angle < 5°. The transparency and anti-wetting property of this coating remained intact even after severe mechanical damages, including sandpaper abrasion, knife scratch test and wiping with gloves, demonstrating exceptional mechanical stability.

Apart from the surface chemistry, physical properties of lubricants such as volatility, viscosity, etc significantly influence the stability of the developed slippery surfaces. For example, Zhao et al. prepared a slippery liquid infused membrane for oil-in-water emulsion separation by infusing different lubricants into the surface modified polyethylene terephthalate nonwoven porous matrix.¹⁵⁶ These selected lubricants mainly fall into two categories depending on their viscosity and volatility - group I consists of less volatile lubricants perfluoropolyether, pump oil, and silicone oil and group II comprises volatile lubricants petroleum ether, cyclohexane. The slippery membrane infused with the group I lubricants can sustain the exposure of 75 °C

for 7 days and continuous water flow for 600 minutes. In contrast, slippery membranes infused with highly volatile group II lubricants transformed into hydrophobic surfaces even at room temperature, due to the rapid evaporation of the lubricant layer.

1.7.2 Surfaces with Micro/Nano Topography

Surface morphology is another crucial parameter in developing liquid repellent surfaces, alongside surface chemistry. Notably, the fabrication of liquid repellent surfaces with special morphological design has recently been introduced to improve the durability of such surfaces. Superhydrophobic surfaces require rough structures that hold meta-stable trapped air layer and the stability of these rough structures cumulatively contributes to the mechanical stability of the surface. However, the simultaneous need for superhydrophobicity and mechanical durability of the surfaces are conflicting from both theoretical and experimental viewpoints. For example, superhydrophobic surfaces with micro/nano pillar or needle-like structures display liquid repellence by minimizing solid-liquid contact area due to the high aspect ratio. However, reduced contact area results in increased localized pressure making the pillar or needle structures more delicate and consequently reducing the mechanical durability of the surface.¹⁵⁷ Hence, further optimization of topography is essential for developing robust and durable liquid repellent surfaces.

‘Crater-like’ inverted pillar/ nanocone design, closed cell micro-geometries were introduced to improve the mechanical durability of superhydrophobic interfaces.¹⁵⁸ In the case of inverted

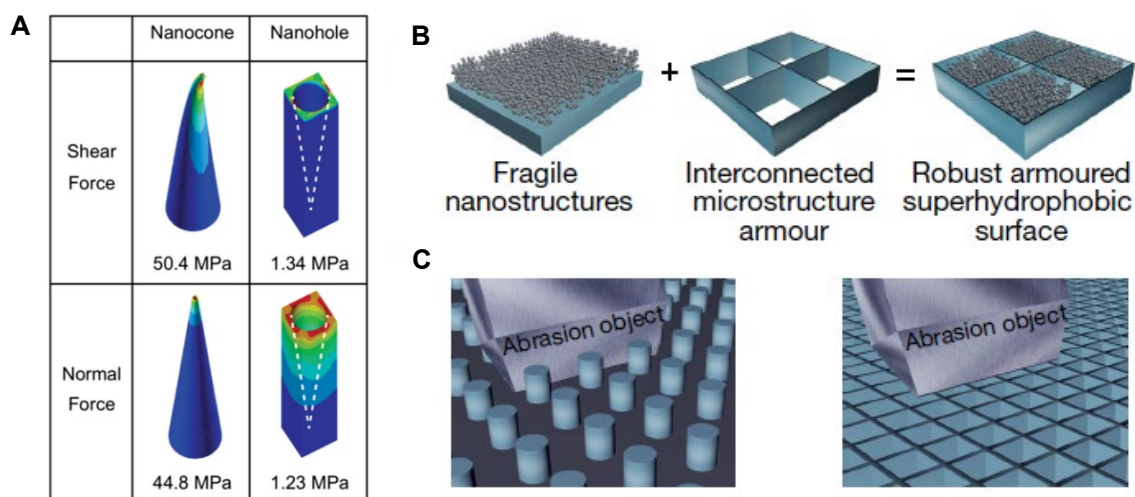


Figure 1.15 A) Distribution of stress in nanocone and nanohole structure. Reproduced from Ref. 158 with permission from copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. B) Schematic showing the design of armoured micro/nanostructured surface. C) Schematic depicting the mechanism of physical abrasions of discrete and interconnected microstructure. Reproduced from Ref. 147 with permission from Springer Nature Limited, copyright 2020.

nanocone, the applied mechanical stress is distributed evenly over the top surface compared to nanocone arrays where stress is mostly concentrated at the conical tip. This even distribution of stress is attributed to the enhanced mechanical stability of the surfaces containing inverted nanocones (Figure 1.15A). However, mostly this single-scale roughness is unable to achieve superhydrophobicity. Hence, designing surfaces with a dual scale of roughness is a common and effective strategy to derive durable and robust superhydrophobic interfaces. Typically, microscale structures combined with nanoscale roughness enhance the durability of surfaces against severe mechanical abrasions. Groten et al. compared the mechanical stability of superhydrophobic surfaces having three different topographies including nano-scale topography, micro-scale topography and a combination of both topographies.¹⁵⁹ Surfaces having a combination of topographies displayed better resistance towards different mechanical loads compared to nano-scale roughness. Wang et al. designed a robust superhydrophobic surface with a combination of both micro and nanostructured design.¹⁴⁷ Nanostructure design provided the water repellence, while microstructure design provided the mechanical durability. The pockets of interconnected microstructures, housing mechanically fragile and water-

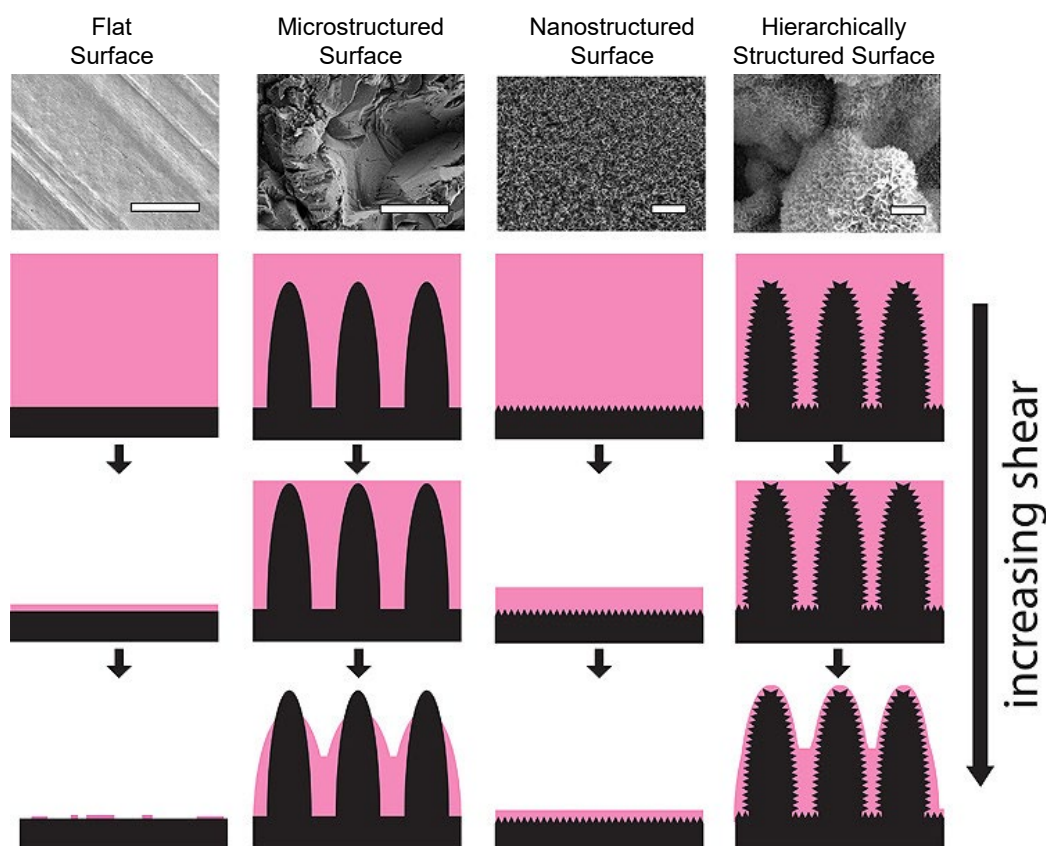


Figure 1.16 Scanning electron microscope images and schematic illustration of lubricant retention ability of surfaces with different morphology including flat surface, microstructured surface, nanostructured surface and hierarchically structured surface under increasing shear stress. Reproduced from Ref. 160 with permission from American Chemical Society, copyright 2013.

repellent nanostructures, act as armour by preventing the removal of nanostructures caused by mechanical abrasions (Figure 1.15B,C). However, in contrast, surfaces with nano-topography are found to be superior compared to microtopography for developing stable lubricant infused slippery surfaces. The infused lubricant can easily leach out from the surfaces having only micro-topography. Kim et al. conducted a comparative study of lubricant holding capacity among surfaces with different morphologies, including flat surfaces, microtopography, nano-topography and hierarchal topography (Fig. 1.16).¹⁶⁰ It was found that only the surface having nano-topography could withstand high shear conditions and displayed unperturbed liquid repellence. The flat surface is unable to hold the lubricant under such conditions due to the absence of capillary force leading to the thinning of the lubricant layer and exposing the underlying substrate. Also, from the microtextured surface lubricant easily leached out from the valleys between larger microscale features under the same acceleration. Hierarchal featured surfaces exhibited behaviour between those with micro and nano-textured surfaces, but, still lubricant leaching from these surfaces compromised the liquid repellence. Hence, the nanostructured surface demonstrated better performance in holding infused lubricant and maintained unaltered liquid repellence under high shear conditions.

1.7.3 Substrate Independent Coating

Developing coating on substrates is a universal solution to prepare substrate-independent liquid repellent interfaces. Hence, the adhesion strength between the coating and substrate will significantly impact the robustness of liquid repellent interfaces. Recently, robust, and durable repellent interfaces have been developed focusing on different strong adhesive interactions such as covalent bonding, cross-linking, introduction of adhesive layer, etc. The covalent bonding strategy has been used effectively to develop superhydrophobic coatings on fabrics, sponges, flat substrates, etc. Mostly, silanols, silane-derived chemicals, epoxide group containing molecules, etc are frequently utilized to form covalent bonds with substrates possessing hydroxyl groups. Baidya et al. developed a durable superhydrophobic coating on cellulose nanofiber through covalent modification of the cellulose nanofiber with two different silane containing molecules—1H,1H,2H,2H-perfluorooctyltriethoxysilane and 3-(2-aminoethylamino)propyltrimethoxysilane (Fig. 1.17A-D).¹⁶¹ Nevertheless, the substrates lacking reactive functional groups need pre-treatment by different methods such as plasma etching, chemical etching, UV light irradiation, and ozone treatment to introduce chemical functionality. Recently, SLIPS has been developed by covalently immobilizing lubricants on smooth surfaces to improve the durability of such surfaces further. Wang et al. developed an

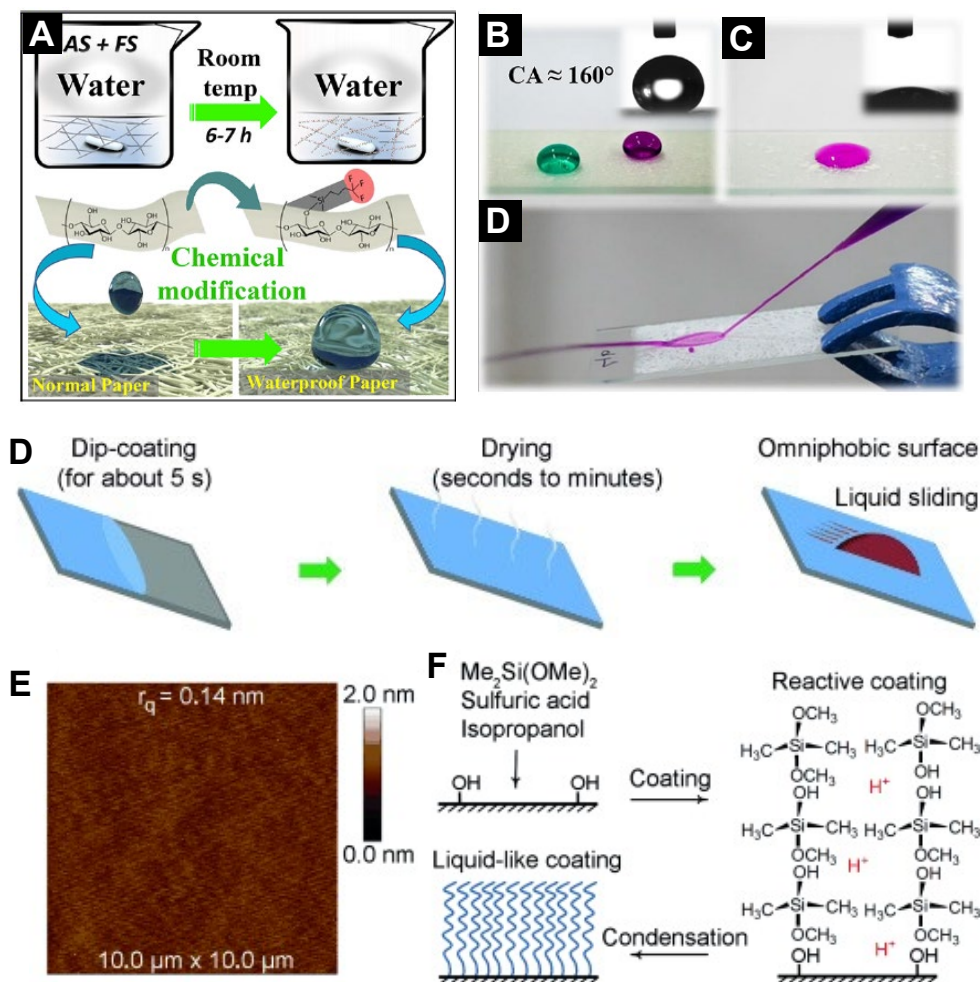


Figure 1.17 A) Schematic representing the fabrication of superhydrophobic cellulose nanofiber (CNF) based superhydrophobic coatings. B, C) Photographs and contact angle images of beaded water droplets on superhydrophobic coated substrate (B) and hydrophilic native CNF coated substrate (C). D) Photographs representing the bouncing of water jet from superhydrophobic coated glass substrate. Reproduced from Ref. 161 with permission from American Chemical Society, copyright 2017. D) Schematic illustrating the fabrication steps of omniphobic slippery coating. E) Atomic force microscopy (AFM) image of the slippery coated surface. F) Formation of the omniphobic coating through acid-catalyzed polycondensation of dimethyldimethoxysilane. Reproduced from Ref. 162 with permission from copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

omniphobic slippery interface by acid catalyzed polycondensation of dimethyldimethoxysilane following the dip coating method.¹⁶² The developed coating remained efficient in repelling liquids having a wide range of surface tensions and displayed excellent thermal stability (Fig. 1.17D-F). In addition to the covalent bonding based method discussed above, durable and robust liquid-repellent interfaces have been successfully synthesized following other approaches such as the cross-linking based approach, adhesive layer formation, etc.

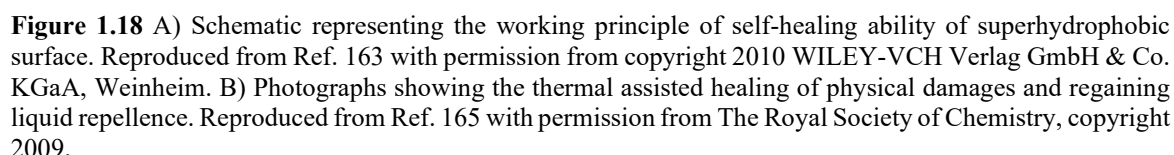
1.7.4 Self-healing Ability

In the presence of continuous exposure to extreme abrasive conditions, liquid-repellent interfaces undergo physical damage and subsequently lose their anti-wetting property. Smart

superhydrophobic interfaces with self-healing ability can be a promising alternative to tackle this problem. Typically, two approaches i.e., regeneration of surface chemistry and restoration of topography are followed to heal physical damages and restore liquid repellence of such surfaces.

In nature, lotus leaf has a unique ability to maintain water repellence at the damaged portion by regenerating the epicuticular wax layer. Taking inspiration from nature, several superhydrophobic interfaces with self-healing ability have been developed through the regeneration of surface chemistry. For example, Li et al. developed a self-healable superhydrophobic coating following two steps- 1st step involved the preparation of rigidly flexible porous polymeric network following layer-by-layer deposition of poly(allylamine hydrochloride) and sulfonated poly(ether ether ketone) with poly(acrylic acid) (PAA) and the 2nd step involves the chemical vapour deposition of low surface free energy 1H,1H,2H,2H-perfluorooctyl-triethoxysilane molecule on the porous network.¹⁶³ This porous network served as a reservoir for excess fluorosilane molecules in the bulk, acting as a healing agent (Fig. 1.18A). When the low surface energy top layer of the superhydrophobic coating was removed due to chemical abrasions, the healing agent migrated from the bulk to the surface under appropriate stimuli, regenerating the surface chemistry and regaining native the water repellence. Another essential criterion of superhydrophobic surfaces is their topography. Physical damage can induce morphological change leading to the compromise of liquid repellence. To combat these challenges, recently smart shape memory polymers and elastic materials with the ability to restore the topography are being used to develop superhydrophobic interfaces. Lv et al. utilized a shape memory epoxy-based polymer to prepare a micro/nanotextured superhydrophobic interface.¹⁶⁴ The morphology of the superhydrophobic surface can be reversibly controlled between permanent and damaged states, resulting in the restoration of extreme water repellence.

In addition to superhydrophobic interfaces, infused lubricant layers on slippery surfaces can heal minor physical damages caused by abrasions and facilitate the quick restoration of liquid repellence of the damaged surface. Generally, liquid lubricants can easily flow to the damaged region of the surface due to their fluidic nature and quickly refill the damaged portion at room temperature. However, liquid lubricant-infused surfaces face durability issues arising from the leaching out and evaporation of lubricant. Recently, there have been some reports on slippery surfaces that address this concern by using solid thermo-responsive low surface energy waxy materials instead of liquid lubricants. These hydrophobic waxy materials form the top infused



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1.8 Motivation and Objectives

Liquid repellent surfaces have attracted significant research interest due to their potential applications in several fields related to energy, environment and health.^{15,16,166,167} Though tremendous progress has been made in the development of liquid repellent surfaces but poor durability and robustness restricted their practical applications and industrialization.^{57,133,168,169} Micro/nanostructure and low surface energy are two essential parameters contributing to the water-repellent properties of superhydrophobic surfaces.⁵⁹ The combination of these two parameters helps to lock air cushion within the grooves of these rough structures, and water droplets readily roll off from the surface. However, micro/nanostructures of these artificially developed surfaces are susceptible to mechanical abrasions.⁵⁷ As a result, these surfaces easily lose their water-repellent properties when exposed to different physical abrasions, limiting their life span and real-life practical applications. Additionally, slippery surfaces are typically prepared by infusing liquid lubricant into a porous micro/nanostructured network.^{16,53} Generally, low surface energy liquids such as perfluoropolyethers or other perfluorinated liquids are used as lubricants, but these lubricants are highly expensive, toxic, and environmentally harmful. Silicon oils are also used as an alternative lubricant. However, silicon oil fails to slide low surface tension liquids, and it can easily leach out, compromising the slippery property of the surface. Mostly, this developed lubricant infused slippery surfaces remain thermodynamically unstable.¹⁶⁸ Although significant progress has been made to enhance the robustness and durability of liquid repellent superhydrophobic and slippery surfaces, till now the number of research articles addressing the robustness and durability of liquid repellent surfaces is considerably less in the relevant literature.^{57,133}

To improve the robustness and durability, a few approaches have been introduced in the literature, as discussed in the earlier section. Surfaces with special structures including closely packed nanostructures, similar rough structures, combinations of micro/nanostructures, etc have been designed to improve the robustness of superhydrophobic surfaces.^{139,147-160} Also, increasing the adhesion strength between coating and substrate, and introducing self-healing ability are some alternative approaches to enhance the durability of liquid repellent coatings.¹⁶¹⁻¹⁶⁵ However, while focusing on durability, these earlier reported approaches lacks the ability to customize other relevant properties -including mechanical property and adhesion property, etc. In addition, to enhance the robustness of lubricant infused slippery surfaces, several methods such as organogel networks or ionic liquids as lubricants, etc have been used to deal with the problem of lubricant leakage or volatilization.¹⁷⁰⁻¹⁷² However, lubricant still can leach out from

the surface and lead to contamination of the beaded liquid on such surface.^{173,174} Hence, further designs are required for developing durable liquid repellent surfaces for meaningful integration of other relevant physical properties including — mechanical property, fluorescence, water adhesion, etc.

In response to these current challenges, in this thesis work, I have utilized a facile and catalyst-free 1,4-conjugate addition reaction between amine and acrylate functional groups of selected small molecules to develop robust and durable liquid-repellent interfaces (Fig. 1.19A, B).

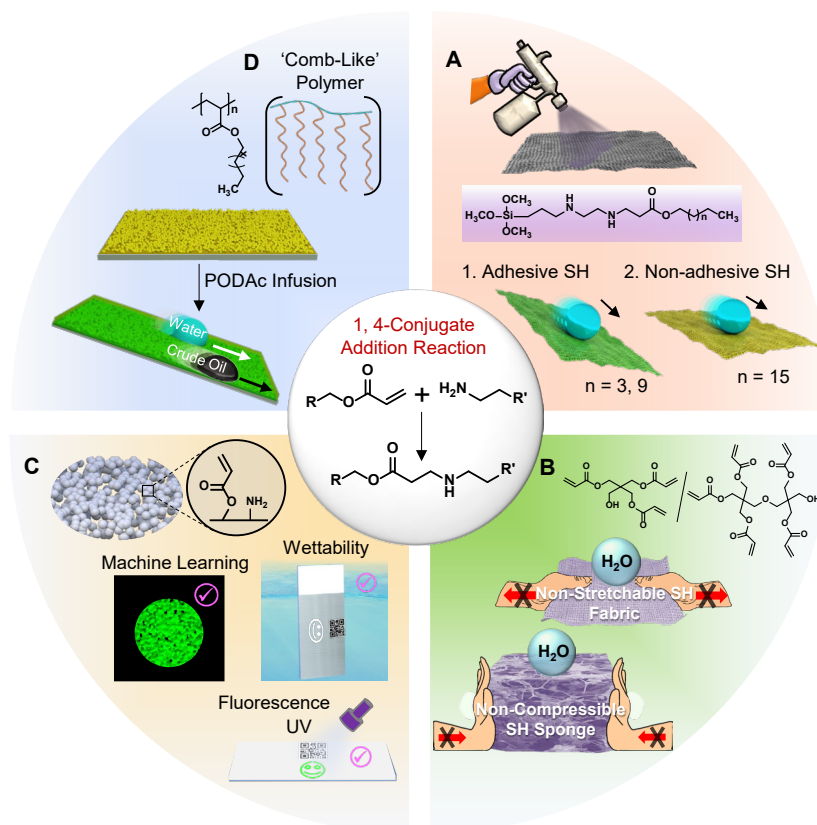


Figure 1.19 Schematic illustration of the utilization of 1, 4-conjugate addition reaction for developing different liquid repellent polymer coated surfaces, including — A) tailored superhydrophobicity on fibrous and porous substrates, B) customization of mechanical properties of stretchable and compressible substrates with enhanced durability, C) dual chemically functionalizable porous polymeric coating for multilevel anti-counterfeiting application, D) solid lubricant infusion into the porous network for developing amphiphobic coating.

Choice of small molecules and appropriate cross-linker in the reaction mixture simultaneously modulated the mechanical property and water wettability of coated surfaces. This facile approach was exploited to achieve superhydrophobic coating for potential applications in water remediation, anti-fouling, self-cleaning, etc. A covalently cross-linked gelation process is introduced utilizing a 1,4-conjugate addition reaction between selected non-fluorinated reactants to customize the mechanical property and water wettability of the selected deformable and stretchable substrates at ambient conditions. Further, the same 1,4-conjugate addition

reaction was followed to prepare a dual chemically functionalizable porous polymeric utilizing a different sol-gel conversion process and subsequent post-chemical modulations were employed to associate fluorescence superhydrophobicity and tailored water adhesion. This chemically functionalizable polymeric coating with a combination of physically unclonable porous topography and distinct physiochemical properties is utilized to develop a multilevel anti-counterfeiting interface (Fig. 1.19C). Further, to combat the challenge of lubricant leaching and stability of lubricant infused slippery surfaces, a completely different strategy was adopted where a solid crystalline ‘comb-like’ phase transitioning polymer was used as a lubricant. A porous polymeric network with different morphology was prepared using the above-mentioned sol-gel chemistry. Infusion of the ‘comb-like’ polymer into this porous matrix resulted in a non-fluorinated, self-healable, substrate independent, durable amphiphobic solid slippery coating (Fig. 1.19D).

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Chapter 2: Small Molecules Derived Tailored-Superhydrophobicity on Fibrous and Porous Substrates—with Superior Tolerance

In the past, different approaches were adopted to prepare superhydrophobic interfaces for demonstrating various prospective applications, where different polymers or nanomaterials are associated for achieving appropriate hierarchical topography and essential chemistry. The commonly used deposition solutions consisting of polymer or nanomaterials prepared in a specific solvent have poor shelf-life. Moreover, the unavailability of robust and optically transparent superhydrophobic coating following a scalable, rapid and single-step deposition process remained a bottleneck problem for its various prospective and relevant applications at real-world scenarios. Here, a catalyst-free 1, 4-conjugate addition reaction between distinct and strategically selected small molecules allowed to preparation of an active deposition solution with prolonged (200 days) shelf-life in various and commonly used reaction media. The small molecules derived deposition solution allowed a rapid and scalable synthesis of abrasion tolerant, optically transparent (99.2%) superhydrophobic coating on different relevant fibrous and porous substrates—following either dip-coating or spray coating process. Further, the appropriate choice of small molecules and the concentration of deposition solutions controlled adhesive interaction (from 24 μN to 204 μN) and hydrophobicity (from $\sim 134^\circ$ to 160°) of the small molecule derived coatings. The entirely small molecules derived bio-inspired coating sustained various physical/chemical abrasive exposures including knife test, repetitive sandpaper abrasion, tensile deformation, adhesive tape peeling, washing, ironing, and prolonged (300 days) UV irradiation, sea water, river water etc. Such interfaces were successfully extended for different practically relevant applications including self-cleaning, oil/water separation, no-loss transfer and mixing of aqueous droplets etc. Moreover, the superior shelf-life of the deposition solution and liberty for selecting different reaction media makes this design exceedingly elegant for industrial scale-up in near future.

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2.1. Introduction

Nature-inspired extremely water-repellent interface (with water contact angle above 150°) widely recognized as superhydrophobic surface holds immense potential for various practically relevant applications.¹⁻¹⁰ Over the last two decades, various approaches have been introduced for co-optimizing the appropriate hierarchical topography and essential low surface energy that conferred the extreme aqueous repellency, where the hydrophilic hierarchical features were mostly topped with low surface energy coating.¹⁻¹⁰ Most of these reported materials suffered from practically relevant durability challenges.^{11,12} Nevertheless, a few seminal designs—including self-healing coatings, candle-shoot derived bulk coatings, multilayered porous coatings, multi-fluorination reaction and ‘micro-armour’ topography based mechanically durable coatings paved a basis for developing tolerant superhydrophobic coating on flat objects (geometrically less complex) that is capable of sustaining under various harsh exposures.¹³⁻²¹ Unfortunately, most of these special designs for developing artificial superhydrophobicity either followed a complex and laborious fabrication process or suffered from scalability challenges.¹³⁻²¹ In the recent past, various fibrous and porous substrates were strategically integrated with bioinspired wettability for developing different functional and smart materials for a wide range of prospective applications in outdoor settings.²²⁻³⁸ While, the superhydrophobic fabrics were extended for developing wearable and self-powered human motion sensors, blood-repellent coating, microwave radiation absorption, water proof capacitor, UV-shielding and so on,^{24,28-31} the superhydrophobic sponges were successfully applied to prepare water proof pressure sensor, under water gas bubble collector, electrode for CO₂ reduction and oil/water separation etc.³²⁻³⁸ The earlier reported durable superhydrophobic coating approaches that demonstrated on flat substrate are often less-appropriate to coat geometrically complex fibrous and porous objects—three dimensionally. So different other strategies were introduced to decorate fibrous and porous substrates with non-adhesive superhydrophobicity. In general, various polymer and nanoparticle-based approaches were adopted to coat fibrous and porous substrates—but in most of the cases, the reported superhydrophobic coatings failed to survive under prolonged and severe exposures of different complex aqueous phases and physical abrasions.^{1, 2, 6, 15, 39-48} Another important aspect related to this bio-inspired water wettability is the poor shelf-life of the deposition solution and the limited choice of solvent/medium to prepare the deposition solution. The polymer and nanoparticle-based reported deposition solutions generally required a specific solvent/mixture of solvents due to their limited solubility and dispersity in a

certain medium, and such deposition solutions inherently suffered from short shelf-life, which likely to impose an unavoidable challenge on the process of industrial scale-up of reported superhydrophobic coatings. In the relevant literatures, very few reports have been introduced, where the shelf-life of deposition solutions have been studied.^{22–27} However, the shelf-life of the deposition solutions mostly remained poor. In addition to this, most of the earlier reported approaches that provided superhydrophobic coating on fibrous and porous substrates^{22–31} lacked the ability to tailor different and desired water wettability following a single step deposition process. The ability to achieve tailored-superhydrophobicity would be useful for droplet manipulations—including the no-loss transport and mixing of tiny water droplets and so on. Hence, a design of deposition solution that accounts for all the relevant and essential characteristics (mentioned in Figure 2.1) related to bio-inspired wettability—including prolonged shelf-life, comprehensive (both physical and chemical) durability, high optical transparency and tailored-

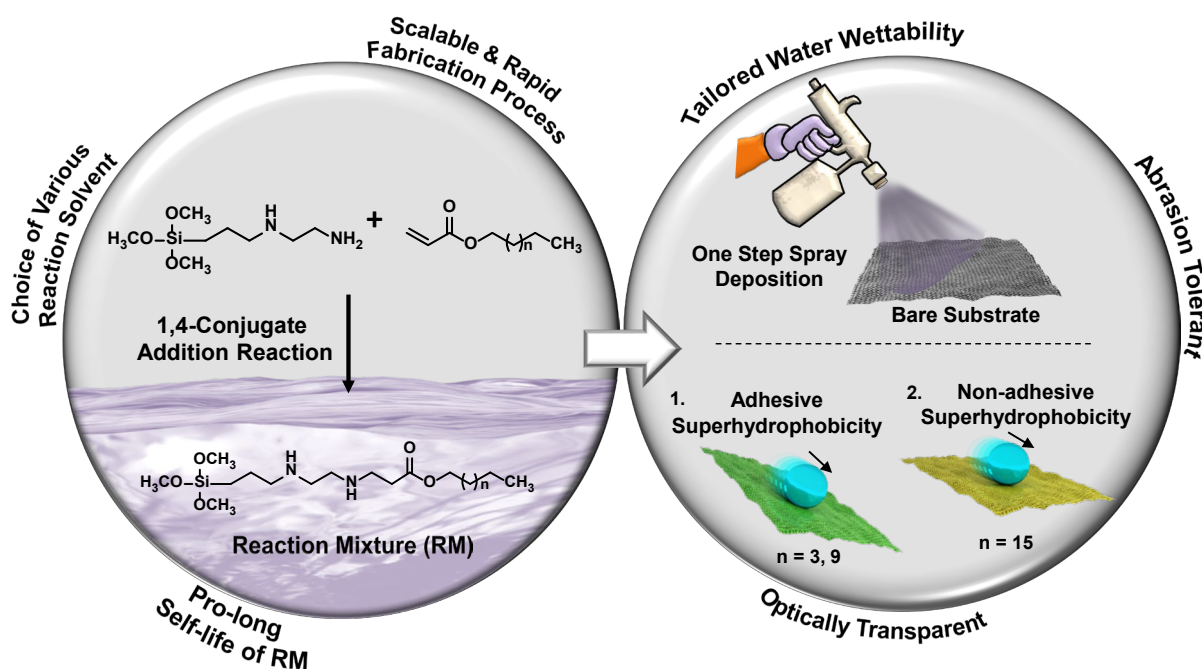


Figure 2.1 Illustrating the key features of the small molecules derived superhydrophobic coating. An abrasion tolerant, optically transparent, tailored water wettability was achieved through the rational use of 1,4-conjugate addition reaction between selected small molecules—alkylacrylate and [3-(2-Aminoethylamino)propyl] trimethoxysilane in a wide range of volatile organic solvents under ambient conditions. The choice of various reaction solvents, prolonged shelf-life of reaction mixture, rapid and facile deposition process are other important features of the current design.

superhydrophobicity through facile, scalable and rapid synthesis process would be appropriate for more realistic and diverse applications.

In this current design, two different types of small molecules (Figure 2.1)— 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS) and alkyl acrylate are unprecedentedly reacted through 1,4- conjugate addition reaction to prepare an active deposition solution for developing a a) fluorine-free b) abrasion tolerant and c) optically transparent (99.2%) superhydrophobic coating following d) a simple, rapid and single step deposition process. As the deposition solution is derived from small molecules, e) a wide range of volatile organic solvents were successfully selected to prepare adequate deposition solution—which f) remained active for 200 days, where the ageing of deposition solution has minimal impact on preparing non-adhesive superhydrophobic coating. Additionally, the judicious selection of reactants and the concentration of deposition solution allowed to tailor g) the water wettability (from $\sim 134^\circ$ to 160°) and h) adhesive interaction between the superhydrophobic coating and beaded water droplet. The synthesized interfaces were successfully extended for proof of concept demonstrations of self-cleaning, energy efficient and environmentally friendly oil/water separation and no-loss transfer and mixing of aqueous droplets.

2.2 Experimental Section

2.2.1 Materials Required

3-(2-aminoethylamino)propyltrimethoxysilane, octadecyl acrylate, hexyl acrylate, dodecyl acrylate, sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB), triton x-114, rhodamine 6G (Rh-6G), methylene blue, Nile red dye were obtained from Sigma Aldrich (Bangalore India). Ethanol was purchased from TEDIA company (United States of America). Propanol, butanol, pentanol, hexanol, and heptanol were purchased from Alfa Aesar, India. Sodium chloride (NaCl), magnesium chloride (MgCl_2), calcium chloride (CaCl_2), and magnesium sulphate (MgSO_4) were purchased from Emparta (Merck Specialties Private Limited). Toluene, acetone, dichloromethane (DCM) and chloroform were obtained from Merck Life Science Pvt Ltd (Bangalore, India). Polyurethane fabric was purchased from Amazon India. Melamine formaldehyde (MF) foam was purchased from AR Acoustics LLP Maharashtra. UV cabinet used for continuous UV exposure was purchased from Relitech (Bengaluru, India). Diesel and petrol were obtained from the nearest Indian oil petrol pump in Guwahati (Assam, India). Motor oil was

obtained from Castrol India Limited. Kerosene oil, cotton, adhesive tape, sandpaper, knife, wool fabric, polyester fabric, lycra fabric, jute fabric, and nonwoven fabric were procured from a local shop in Guwahati city (Assam, India). Milli-Q grade water was used for all experiments.

2.2.2 Characterization

The contact angle measurements were taken using the KRUSS Drop Shape Analyser-DSA25 instrument with an automatic liquid dispenser at ambient conditions. Advancing and receding water contact angles were measured at four different locations for each sample. Field Emission Scanning electron microscope (FESEM) images were acquired using Sigma Carl Zeiss scanning electron microscope (samples were coated with a thin layer of gold before imaging). Fourier transform infrared attenuated total reflectance spectra (FTIR-ATR) were recorded using the PerkinElmer instrument. UV–Vis spectra were obtained using the Perkin-Elmer Lambda 750 (UV/Vis/NIR Spectrometer). Digital pictures were acquired using a Canon Power Shot SX420 IS digital camera. Adhesive force was measured using a fully automated force tensiometer (Kruss GmbH, K100).

2.2.3 Fabrication of Superhydrophobic Interfaces

Primarily, a reaction mixture was prepared by mixing solutions (the concentration of each reactant was 30 mM) of 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS) and octadecylacrylate (ODAc) in ethanol and then the solution was shaken vigorously for 10 min. Briefly, a 5 mL reaction mixture was spray deposited on the fibrous substrate (10 cm × 10 cm) from a 10 cm distance using a commercial spray bottle (nozzle diameter ~ 400 µm) and kept for drying for 4 h in a hot oven (70 °C) to obtain superhydrophobicity. Later, the anti-wetting property was examined through visual inspection and contact angle measurements.

2.2.4 Physical and Chemical Durability

Various standard physical and chemical durability tests were performed on the superhydrophobic fabrics. The details of each experimental procedure are explained in the following sections.

2.2.4.1 Sand Paper Abrasion Test

In sandpaper abrasion, 400-grit sandpaper (3 cm × 1 cm) was manually abraded across the superhydrophobic fabric (5 cm × 1.5 cm) for 100 cycles —with an applied pressure of 66 kPa and

an average speed of ~ 16.6 cm/s. After this test, the water wettability was examined with visual inspection and contact angle measurements.

2.2.4.2 Adhesive Tape Peeling Test

In this abrasive test, a freshly exposed adhesive tape was placed on the superhydrophobic fabric ($3\text{ cm} \times 1\text{ cm}$) with an applied pressure of 66 kPa for 60 sec. Then, the adhesive tape was manually peeled off from the fabric and the freshly exposed interface was examined using contact angle measurements. This test was repeated for 100 times.

2.2.4.3 Sand Drop Test

Firstly, a freshly synthesized superhydrophobic interface was attached to a glass slide inclined with a 45° tilting angle, and then 300 g of sand grains were dropped from 25 cm. After performing the sand drop test, the embedded superhydrophobic property was examined with contact angle measurements and visual inspections.

2.2.4.4 Knife Scratch Test

The superhydrophobic fabric was scratched with a fine knife several times in different directions. The water wettability on the physically damaged interface was thoroughly characterized by contact angle measurements.

2.2.4.5 Tensile Deformation Test

The superhydrophobic interface was subjected to a tensile strain up to 150% for repetitive 1000 cycles and afterwards, the water contact angles were measured at regular intervals to examine the impact of physical deformation on the bio-inspired wettability.

2.2.4.6 Exposures to Various Complex Aqueous Environments and UV Radiation

The superhydrophobic interfaces were exposed to different aqueous environments including artificial seawater (solution of 0.226 g MgCl_2 , 0.325 g MgSO_4 , 2.673 g NaCl , and 0.112 g CaCl_2 in 100 mL of deionized water), river water (Brahmaputra River, Assam, India) for 250 days. The superhydrophobic coated fabric was also exposed to UV irradiation (254 nm and 365 nm) for 250 days. The anti-wetting property was examined through contact angle measurements at regular time intervals.

2.2.4.7 Thermal Stability

The superhydrophobic fabric was kept in boiling water for 50 h. After that, the fabric was then rinsed with fresh water and dried at room temperature. The superhydrophobic fabric was also kept in an oven at 80 °C for 30 days and at -20 °C for 7 days. The anti-wetting property was examined through contact angle measurements at regular time intervals.

2.2.4.8 Laundering and Ironing Test

The washing durability was examined by a standard procedure (AATCC Test Method 61–2006 test No 2A) where the superhydrophobic fabric was laundered at 40 °C for 45 min in presence of 0.37 wt% SDS surfactant. The superhydrophobic fabric was also repetitively ironed around 180 °C for 200 times. After that, the anti-wetting property of the fabric was thoroughly characterized using contact angle instruments.

2.2.5 Filtration Based Oil–Water Separation

The filtration-based oil–water separation was demonstrated by strategic use of the superhydrophobic interface. A lab-made prototype was developed by using one end opened glass tube which was blocked with superhydrophobic fabric and a surface hole was also made at another end of the glass tube for pouring the oil–water mixture. A variety of oil–water mixtures were poured within this prototype where only the oil phase passes through the superhydrophobic fabric and is collected in a cleaned beaker. The oil separation efficiency was calculated by using the following formula: $\eta = \{(W_2)/(W_1)\} \times 100 \%$

Where η is the oil separation efficiency (%), W_1 is the summation of the initial weight of oil and superhydrophobic fabric taken before separation and W_2 is the summation of the final weight of the obtained oil and used superhydrophobic interface after separation.

2.2.6 Absorption Based Oil–Water Separation

First, a droplet (2 mL) of light oil was placed on top of the water interface in a glass petri dish and thereafter, a superhydrophobic sponge was placed at the oil/water interface. The oil phase was selectively absorbed by the superhydrophobic sponge within a minute. The absorbed oil was collected separately by manually squeezing the sponge. The absorption capacity was calculated using the following formula:

$$Q = (m_2 - m_1) / m_1$$

Where m_1 and m_2 are the weight of the superhydrophobic sponge before and after oil absorption.

2.3 Results and Discussions

2.3.1 Small Molecules Derived Bio-Inspired Coating and Its Characterizations

In the past, a facile and catalyst-free 1,4-conjugate addition reaction between branched poly(ethyleneimine) and dipentaerythritolpenta acrylate has been extended to develop various functional polymeric coatings mostly following multistep deposition processes.^{19,49–52} In the recent past, 1,4-conjugate addition reaction has been extended to develop a chemically reactive and polymeric nanocomplex (CRPNC) that is loaded with residual acrylate groups.⁵³ The ageing of CRPNC solution for 3.5 h led to the formation of self-standing gel through covalent crosslinking between residual functional groups.⁵³ A further selection of external solvent and the addition of salt accelerated the gelation of CRPNC dispersion.^{54,55} Such CRPNC with a short shelf-life was strategically extended to prepare the chemically reactive polymeric coating, where the choice of solvent and additives played a crucial role in achieving stable coating.^{19,26–27} An additional and appropriate post covalent modification of such chemically reactive coating with selected alkyl amines for overnight yielded an optically translucent superhydrophobic coating.^{26,27} Unlike previous reports, in our current approach, 1,4-conjugate addition reaction is rationally extended with commercially available and economically viable two small molecules—AEAPTMS and octadecylacrylate (ODAc) to develop a reaction mixture with prolonged shelf-life in a wide range of organic solvents which can be utilized for single-step fabrication of superhydrophobic interfaces with tailored adhesive properties. The selected reactants were mixed in the molar ratio of 1:1 in ethanol at ambient conditions, and as expected, amine groups of AEAPTMS spontaneously reacted with the acrylate moiety of ODAc as characterized through standard Fourier transform infrared attenuated total reflectance spectra (FTIR-ATR) analysis.^{19,26,27} During the 1,4-conjugate addition reaction between amine and acrylate groups, the vinyl moiety of ODAc was compromised, whereas the carbonyl moiety remained unaffected during the reaction. At time zero, the FTIR-ATR peaks at 1410 cm^{-1} and 1730 cm^{-1} confirmed the existence of both C–H deformation of β -carbon of vinyl group and carbonyl stretching in the reaction mixture respectively. However, as the reaction proceeds, the IR peak intensity at 1410 cm^{-1} depleted selectively and significantly with respect to the carbonyl stretching at 1730 cm^{-1} , as shown in Figure 2.2A. Moreover, the

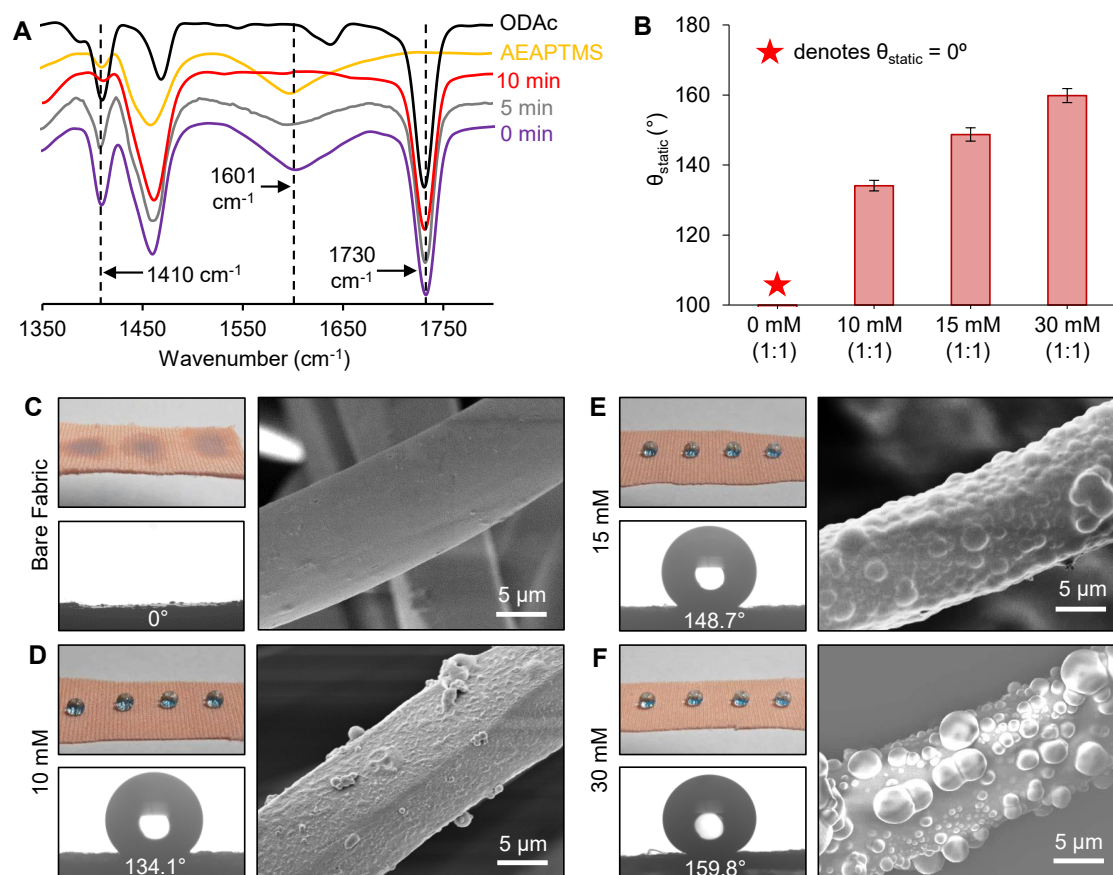


Figure 2.2 Illustrating the reaction between selected reactants and the impact of their compositions on water wettability. A) FTIR-ATR spectra for the individual solution of selected small molecules—octadecylacrylate (ODAc, black) and [3- (2 aminoethylamino)propyl] trimethoxysilane (AEAPTMS, yellow) in ethanol. Further, the FTIR-ATR spectra were recorded for the reaction mixture (1:1) of ODAc and AEAPTMS in ethanol at regular time intervals, including 0 min (blue), 5 min (green) and 10 min (red). In the FTIR-ATR spectra, the IR peaks at 1730 cm^{-1} , 1601 cm^{-1} and 1410 cm^{-1} characterizing the signatures for C = O stretching, primary N–H bending and C–H deformation of the β -carbon of the vinyl group respectively. B) Plots accounting for the changes in static contact angle on the synthesized coatings that were prepared by varying different molar concentrations of selected reactants, where the molar ratio of reactants kept at 1:1. C-F) Digital images, contact angle images of beaded water droplet and FESEM images of the bare fibrous substrate (C) and small molecules derived coatings on the fibrous substrates (D-F), where the deposition solutions were prepared by changing the molar concentrations (10 mM, D; 15 mM, E; 30 mM, F) of the reaction mixture of small molecules.

characteristic IR signature of the N–H bending for primary amine at 1601 cm^{-1} gradually decreased with increasing reaction time. After 10 min duration of the reaction mixture, the significant reduction of the characteristic IR signatures at 1410 cm^{-1} and 1601 cm^{-1} for both C–H deformation of β carbon of vinyl group and N–H bending of primary amine, respectively, validated the

successful 1,4-conjugate addition reaction between two selected small molecules. Next, the reaction mixtures having different molar concentrations (10 mM to 30 mM) were spray deposited on a polyurethane-based inherently hydrophilic (Figure 2.2C) fibrous substrate. On increasing the concentration of reaction mixtures (the molar ratio of reactants kept at 1:1), the spray deposited coating displayed enhanced water wettability (from 134° to 159°) as shown in Figure 2.2B. At the concentration of 30 mM of each of the selected reactants (AEAPTMS and ODAc), the deposition solution I (denoted as DS-1) displayed superhydrophobicity with a water contact angle of $\sim 159^\circ$. The gradual change in reaction concentration of spray deposited solution resulted in an obvious alteration of topography on the selected featureless fibrous substrates, as shown in Figure 2.2C-F. A prominent granular domain with random sizes appeared uniformly on the fibrous substrate for the reaction mixture of small molecules having a concentration of 30 mM, as shown in Figure 2.2F. The presence of such hierarchal features is known to stabilize meta-stable trapped air and contribute to achieving superhydrophobicity.^{56,57} Higher concentrations of reactants resulted in uniformly deposited granular domains, which is essential to confer superhydrophobicity. The reaction mixture of the same reactants (AEAPTMS and ODAc) having the same composition (1:1)—but with lower concentrations (below 30 mM) failed to provide extreme water repellency due to the lack of appropriate topography, as evident from Figure 2.2E, D. The globular domains are less prominent once the concentration of the reactants in the reaction mixtures is reduced to

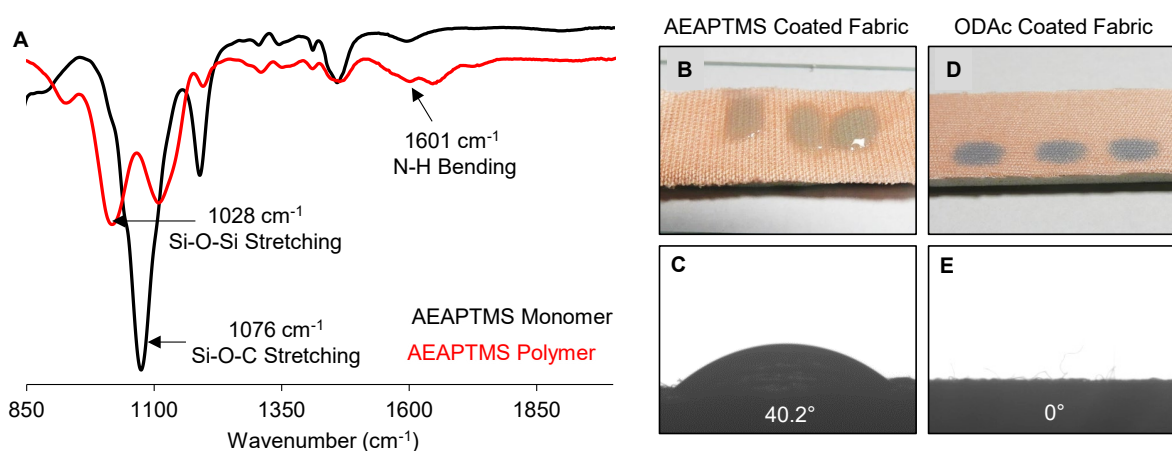


Figure 2.3 A) ATR-FTIR spectra of the solution (black) and dried coating (red) of [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS). The appearance of IR peak at 1028 cm^{-1} for Si-O-Si linkage revealed the polymerization of AEAPTMS during the drying process. B, C) Digital image (B, D) and contact angle image (C, E) of beaded water droplets on AEAPTMS (B, C) and octadecyl acrylate (ODAc) (D, E) coated fabric.

below 30 mM (Figure 2.2E, D). Thus, the concentration of reactants in the reaction mixture played a crucial role in adopting essential topography that conferred superhydrophobicity. In our current design, AEAPTMS is selected as a binder, where the self-polymerization ability during solvent evaporation process as evident from FTIR-ATR spectral study (Figure 2.3A) allowed to achieve durable coating. The appearance of characteristic IR signature at 1028 cm^{-1} for Si-O-Si bridge

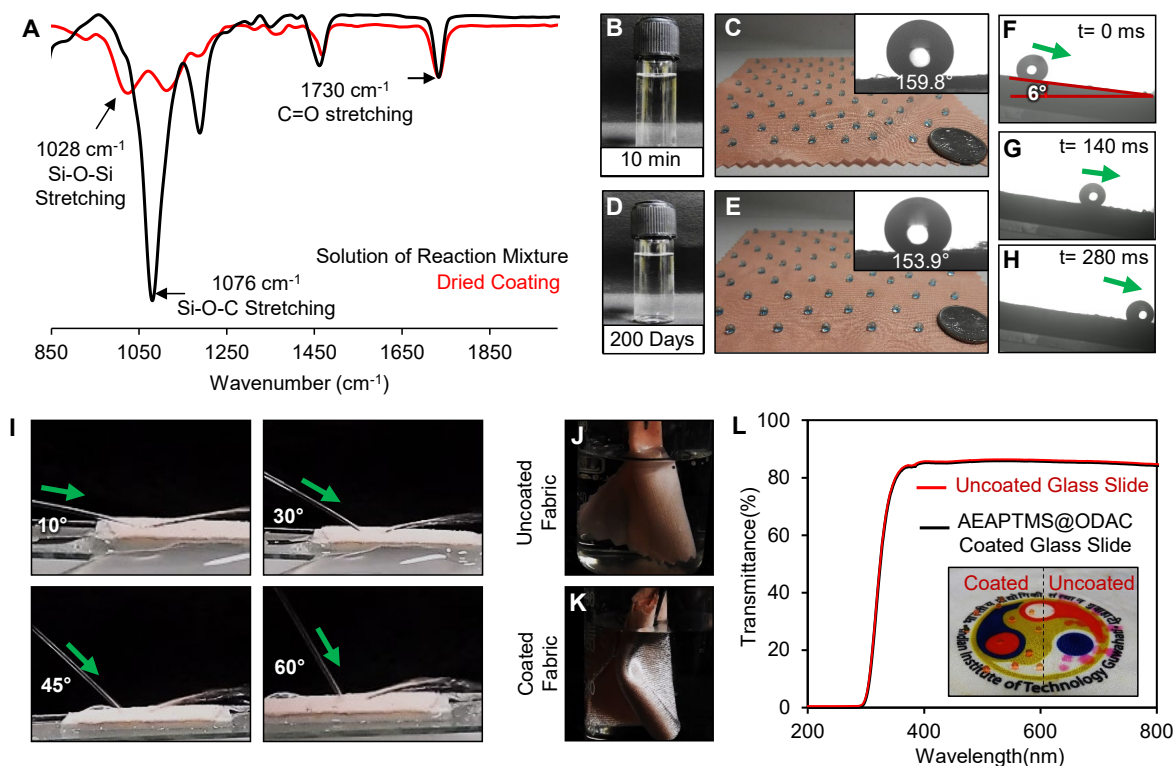


Figure 2.4 A) ATR-FTIR spectra of the reaction solution (black) after storing it for 10 minutes and after drying of the deposited coating (red) of same reaction solution. B-E) Digital images of the reaction mixture of ODAC and AEAPTMS in ethanol after ageing it for 10 min (B) and 200 days (D). C,D) Digital image and contact angle image (inset) of beaded water droplets on the coated fabric, where the reaction mixture spray deposited after storing it for 10 min (C) and 200 days (E). F-H) Demonstration of the rolling of a beaded water droplet (10 μL) on the tilted (6°) superhydrophobic coating that was derived from a 200 days aged reaction mixture of selected small molecules. I) Digital images accounting the bouncing of water jet on the superhydrophobic interface where the incident angle of water jet was gradually varied from 10° to 75° . J, K) Digital images of uncoated (J) and coated superhydrophobic fabric (K) under water, where the shiny interface appeared due to entrapped air layer in the coated, surface whereas uncoated substrate wetted completely. L) Optical transmittance spectra of uncoated (red) and coated (black) glass slide, where coating was achieved by depositing the reaction mixture of AEAPMTS and ODAC. Inset digital image depict our (Indian Institute of Technology Guwahati) institute logo printed fabric with and without coating, where optically transparent and superhydrophobic coating was applied on half of the area (left side of the dotted line) in the image.

confirmed the polymerization process.⁵⁸ However, the deposition of only AEAPTMS (30 mM) and ODAc (30 mM) on the selected hydrophilic fibrous substrate failed to provide extreme water repellence rather the water droplet beaded with a contact angle (CA) of $\sim 40^\circ$ and 0° , respectively (Figure 2.3B-E). Nevertheless, the appropriate association of 1, 4-conjugate addition reaction with the self-polymerization process allowed the single-step co-optimization of essential topography and appropriate chemistry for conferring desired superhydrophobicity. The characteristic IR signature at 1028 cm^{-1} for the Si-O-Si bridge revalidated the successful polymerization of the reaction mixture (black) during the solvent-evaporation process (Figure 2.4A). After ageing of DS-1 for 10 min (Fig. 2.4B), its spray deposition yielded an extremely water-repellent coating, where water droplets beaded with WCA of $\sim 159^\circ$ as shown in Figure 2.4C. Thereafter, the same reaction mixture that was stored in ambient conditions for 200 days was spray deposited (Figure 2.4D, E), and the coating displayed superhydrophobicity with WCA above 150° and roll-off angle 6° as shown in Figure 2.4F-H. Further, a water jet immediately bounced off from the superhydrophobic interface, irrespective of the incident angle, as shown in Figure 2.4I. This result indicated the existence of non-adhesive and robust superhydrophobicity. The entrapment of the external third phase—air, minimized the interaction between the aqueous phase and the bio-inspired coating. The underwater shiny interface revealed the existence of external trapped air in the small molecules

Solvent	t = 0 days		t =200 days	
	$\theta_{\text{static}} (^\circ)$	$\theta_{\text{hys}} (^\circ)$	$\theta_{\text{static}} (^\circ)$	$\theta_{\text{hys}} (^\circ)$
Toluene	161.2 ± 0.6	3.9 ± 0.6	152.4 ± 1.5	5.9 ± 1.2
Ethanol	159.8 ± 0.5	4.5 ± 0.5	151.9 ± 1.2	6.8 ± 1.3
Propanol	158.8 ± 0.8	4.6 ± 0.7	152.5 ± 1.6	7.0 ± 1.1
Butanol	159.5 ± 0.9	3.9 ± 1.1	151.5 ± 0.7	6.8 ± 0.9
Pentanol	158.5 ± 1.1	4.0 ± 1.0	151.4 ± 0.9	6.5 ± 0.8
Hexanol	160.2 ± 1.3	4.7 ± 0.7	150.8 ± 1.1	7.1 ± 1.7
Heptanol	158.2 ± 0.8	4.6 ± 0.6	152.7 ± 1.4	6.6 ± 0.7

Table 2.1 Accounting the water wettability of beaded droplets on superhydrophobic coatings that were prepared using different volatile organic solvents as reaction medium, where the respective reaction mixtures were spray deposited after storing them for 10 min and 200 days, respectively.

derived coating, as shown in Figure 2.4K. As expected, such a shiny interface was not observed for the uncoated substrate (Figure 2.4J). Further, the synthesized superhydrophobic coating remained 99.2 % optically transparent (Figure 2.4L) with respect to bare glass. Our institute (Indian Institute of Technology Guwahati) logo-printed t-shirt was successfully and selectively (left side of the dotted line in the inset image of Figure 2.4L) coated for a visual demonstration of the optical transparency and water repellence of the synthesized coating. Further, the reaction mixtures of AEAPTMS and octadecyl acrylate, which were prepared using various other volatile organic solvents, including acetone, toluene, propanol, butanol, pentanol, hexanol and heptanol, remained capable of providing extremely water-repellent coating. The spray deposition of the respective reaction mixture provided non-adhesive superhydrophobicity with static WCA above

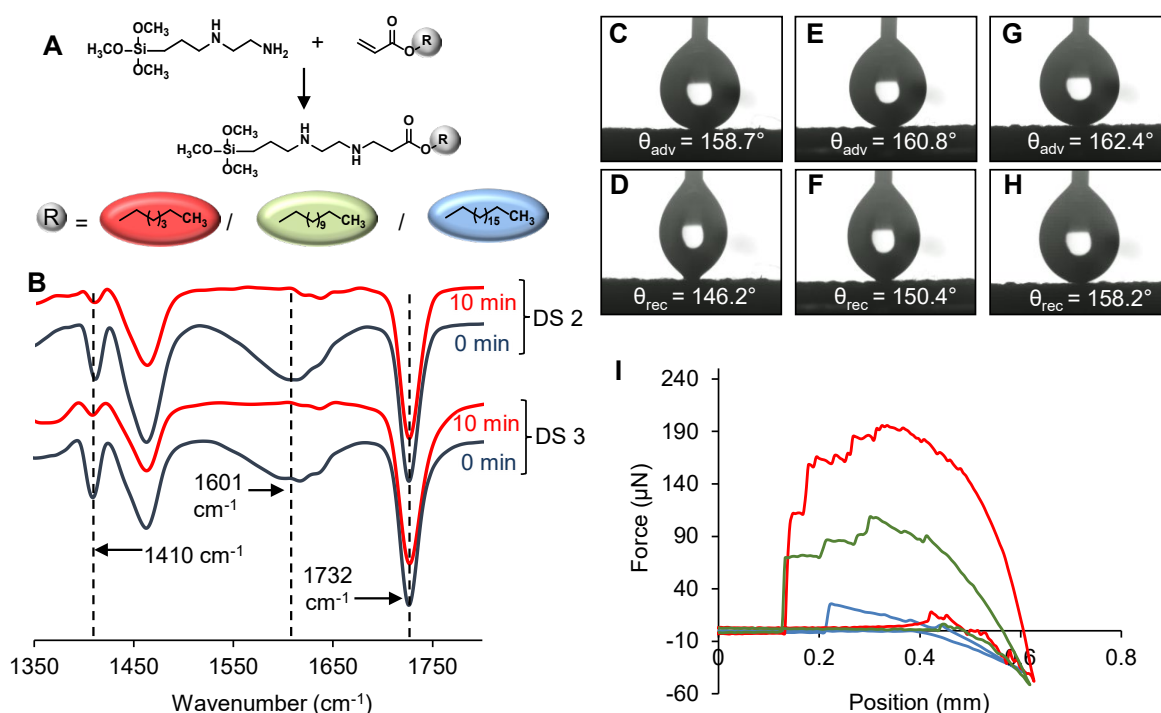


Figure 2.5 Illustrating a facile and single step chemical process for tailoring water wettability. A) Schematic representing the 1, 4-conjugate addition reaction between amine group of [3-(2-aminoethylamino)propyl] trimethoxysilane and acrylate group of different alkyl acrylates (ODAc, dodecylacrylate (DDAc) and hexyl acrylate (HAc)). B) FTIR-ATR spectra of two distinct deposition solutions (DS), labelled as DS 2 (mixture of HAc and AEAPTMS; 1:1) and DS-3 (DDAc and AEAPTMS; 1:1) were recorded at 0 min (blue) and 10 min (red). C–H) Advancing (C, D, E) and receding (F, G, H) water contact angle images of a beaded water droplet on the coated interfaces where the deposition solutions were prepared separately by associating HAc (C, F), DDAc (D, G) and ODAc (E, H) in the respective deposition solutions. I) Adhesion force profiles for the coatings that were individually derived from DS-1 (ODAc and AEAPTMS; 1:1) blue), DS-2 (red) and DS-3 (green), respectively.

150° and contact angle hysteresis below 10°, irrespective of the choice of organic solvents as shown in Table 2.1. Even after 200 days, the same reaction mixtures that were prepared in various organic solvents remained capable of providing bio-inspired superhydrophobic coating as noted in Table 2.1. The HPLC grade organic solvents and low concentration of reactants allowed for suppression of the cross-linking of the siloxane during the storage of the reaction mixture for a maximum of 200 days. Beyond 200 days, the reaction mixture failed to provide non-adhesive superhydrophobicity, rather an adhesive superhydrophobic coating was found. Thus, various volatile organic solvents can be used as reaction mediums for preparing a deposition solution consisting of selected small molecules to achieve bioinspired superhydrophobicity. Next, the adhesive interaction between the bio-inspired coating and beaded water droplet was modulated through the rational selection of alkyl acrylates during the preparation of the reaction mixture as

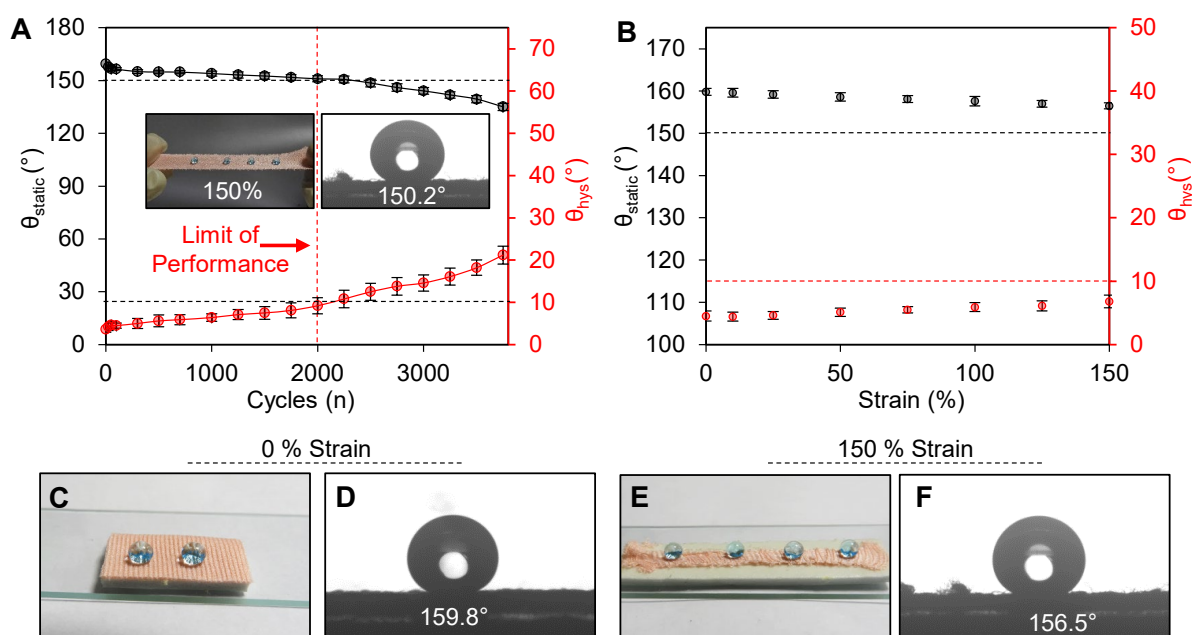


Figure 2.6 A) Plot showing the change in static contact angle (black) and contact angle hysteresis (red) of beaded water droplet on the non-adhesive superhydrophobic coating during the repetitive (3750 cycles; the red dotted line indicating the limit of performance, i.e. 2000 times), tensile (150%) deformation process, and the inset showing the digital image & static contact angle image of beaded water droplets on the superhydrophobic coating after application of repetitive external tensile strain (150%). B) The plots accounting the changes in static contact angle (black) and respective contact angle hysteresis (red) of beaded water droplet on the synthesized superhydrophobic interface during the gradual increase of tensile deformation from 0 to 150%. C-F) Digital images (C, E) and static contact angle image (D, F) of beaded water droplet on non-adhesive superhydrophobic interface after application of 0% (C, D) and 150% (E, F) tensile deformation.

shown in Figure 2.5A. The deposition solutions were obtained by individually mixing hexyl acrylate (HAc; 30 mM) and dodecyl acrylate (DDAc, 30 mM) with AEAPTMS (30 mM), denoted as DS-2 and DS-3. The mutual reaction between these two selected small molecules was verified with standard ATR-FTIR analysis as shown in Figure 2.5B. As expected, within 10 min, the catalyst-free 1,4-conjugate addition reaction between amine and acrylates in DS-2 (HAc and AEAPTMS) and DS-3 (DDAc and AEAPTMS) at ambient conditions led to the depletion of IR signatures for both amine (at 1410 cm^{-1}) and vinyl (at 1601 cm^{-1}) moieties, respectively, as shown in Figure 2.5B. The separate spray deposition of the DS-2 and DS-3 provided tailored superhydrophobicity with different advancing ($\sim 159^\circ$ and $\sim 161^\circ$) and receding ($\sim 146^\circ$ and $\sim 150^\circ$) water contact angles, as shown in Figure 2.5C, E, G and 2.5D, F, H. The adhesive force between the beaded droplet and the superhydrophobic coatings that were derived from DS-2 and DS-3 were found to be $204\text{ }\mu\text{N}$ (red) and $104\text{ }\mu\text{N}$ (green), respectively (Figure 2.5I). The superhydrophobic

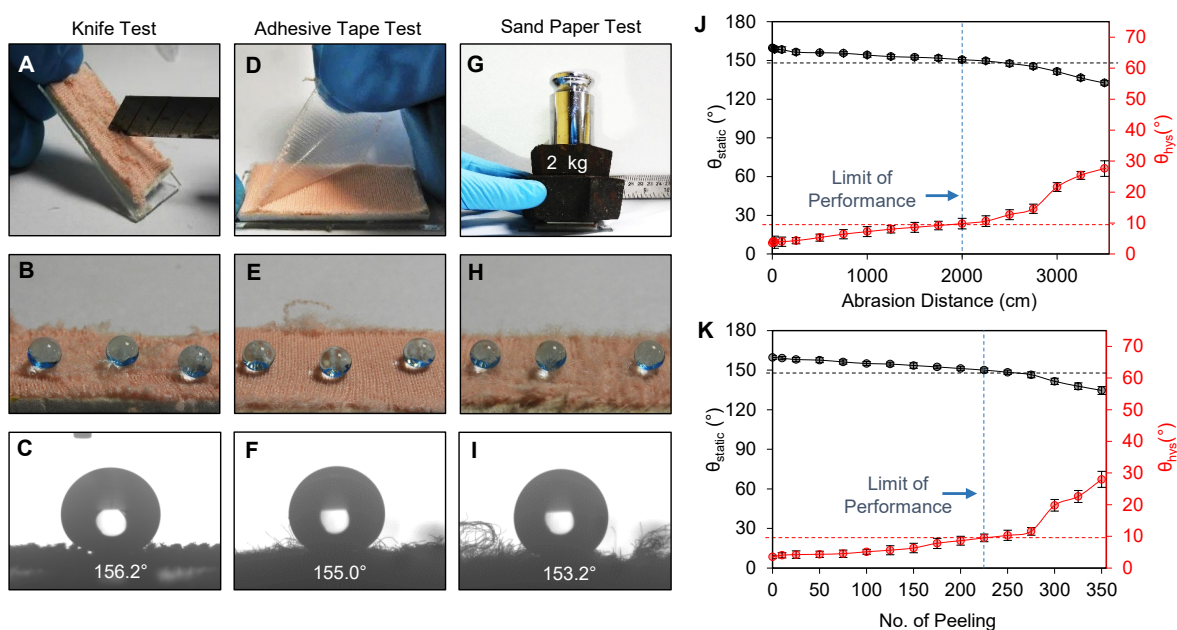


Figure 2.7 A, D, G) Digital images of the experimental setup for knife test (A), adhesive tape peeling test (D), sand paper abrasion test (G). B, E, H) Digital images of the beaded water droplets after performing knife test (B), adhesive tape peeling test (E) and sand paper abrasion test (H). C, F, I) Contact angle images of the beaded water droplets after performing knife test (C), adhesive tape peeling test (F) and sand paper abrasion test (I). J) The plots showing the changes in the static contact angle (black) and respective contact angle hysteresis (red) of beaded water droplet on gradual increment of abrasion distance during the course of sand paper test. K) The plots illustrating the changes in static contact angle (black) and respective contact angle hysteresis (red) of beaded water droplet on the superhydrophobic interface after repetitive exposure to adhesive tape peeling test.

coating derived from DS-1 (having ODAc) displayed a receding water contact angle of 158° (Figure 2.5H) and an adhesive force of $24\ \mu\text{N}$ (Figure 2.5I, blue). Thus, the adhesive force gradually decreased on the association of higher analogues of HAc as shown in Figure 2.5I. The appropriate selection of small molecules allowed adequate chemical optimization—which is important for tailoring both Cassie-Baxter and Cassie-Wenzel transitional states. Such tunable adhesive superhydrophobicity was also extended to demonstrate the controlled mixing and no-loss transfer of aqueous droplets (discussed later in detail).

2.3.2 Investigating the Durability of Synthesized Bio-Inspired Coatings

To investigate the robustness of the synthesized non-adhesive superhydrophobic coating, various standard and practically relevant abrasive tests were performed on the freshly prepared bio-inspired coating.^{11–12} Firstly, the superhydrophobic coating on the stretchable fibrous substrate was exposed to large physical deformation, and the embedded superhydrophobicity remained capable of sustaining a tensile deformation of 150% with static WCA of 156° and contact angle hysteresis

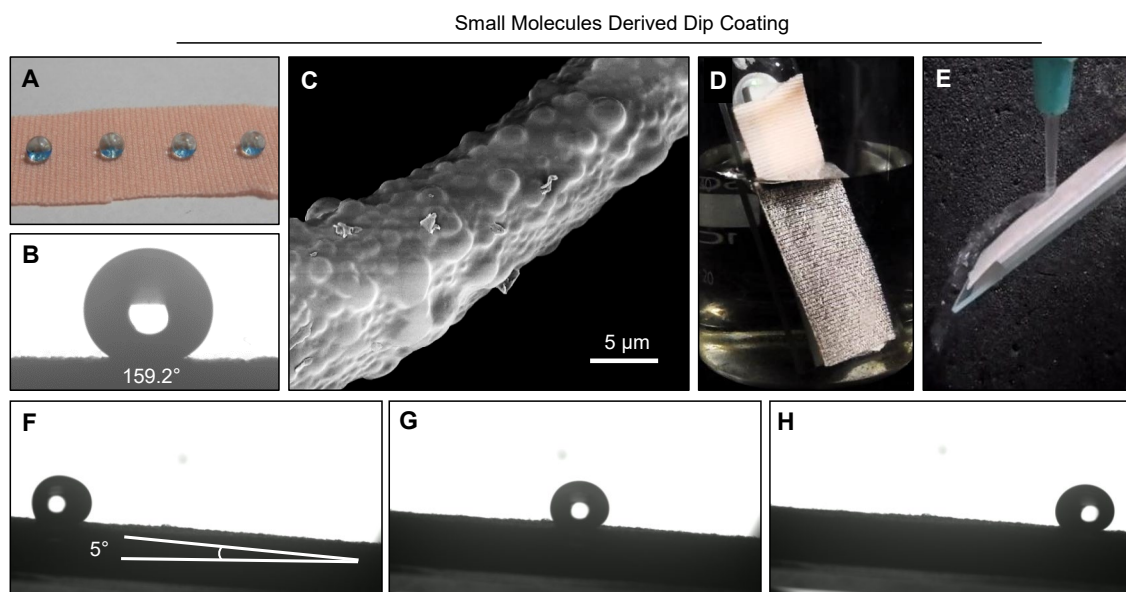
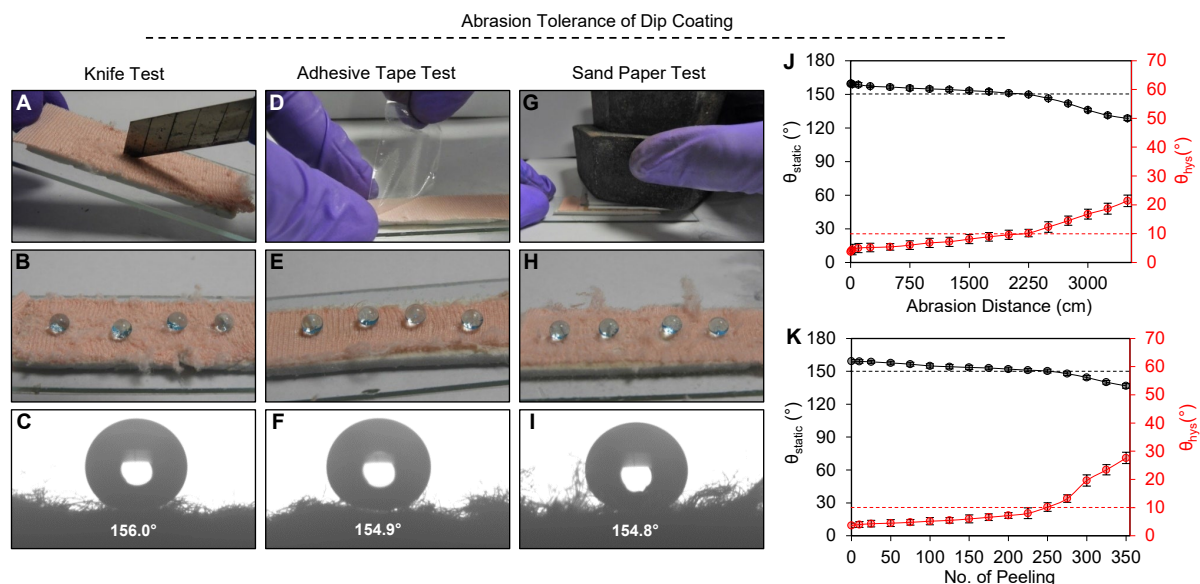


Figure 2.8 A-B) Digital images (A) and contact angle images (B) of beaded water droplet on small molecules derived coated superhydrophobic fabric which was fabricated through dip coating method. C) FESEM images of small molecules derived coated fabric. D) Digital images of superhydrophobic fabric under water which became shiny because of entrapped air layer. E) Illustrating the bouncing of continuous water flow through small molecules derived coated superhydrophobic fabric which was fabricated through dip coating method. F-H) Demonstration of the rolling of beaded water droplet ($10\ \mu\text{L}$) on the tilted (5°) superhydrophobic fabric.



of below 10° , as shown in Figure 2.6A-F. The small molecules derived coating was extended to repetitive tensile deformation (150%) 3750 times. The embedded non-adhesive superhydrophobicity remained intact till 2000 times. Further, any deformation of the coated substrate compromised the embedded superhydrophobicity (Figure 2.6A). Next, the small molecules derived superhydrophobic coating on the fibrous substrate was exposed to successive knife tests (Figure 2.7A), where the physical damages were clearly visible on the synthesized bio-inspired interface. Nevertheless, the water droplets beaded on the physically damaged interface with a static WCA of $\sim 156^\circ$ (Figure 2.7B, C). The as-synthesized superhydrophobic coating was then exposed to an adhesive tape peeling test, where a freshly exposed adhesive surface was placed on the bio-inspired coating with an applied load of 66 kPa for 60 s before peeling off the applied tape from the superhydrophobic interface as shown in Figure 2.7D-F. Such adhesive tape peeling

test was repeated 350 times (Figure 2.7K). The synthesized coating failed to perform after repeating the adhesive tape peeling test above 250 cycles (Figure 2.9K). Thereafter, an abrasive sandpaper was rubbed on the synthesized superhydrophobic interface with an applied load of 66 kPa (Figure 2.7G-I), and the water wettability was investigated by increasing the sandpaper

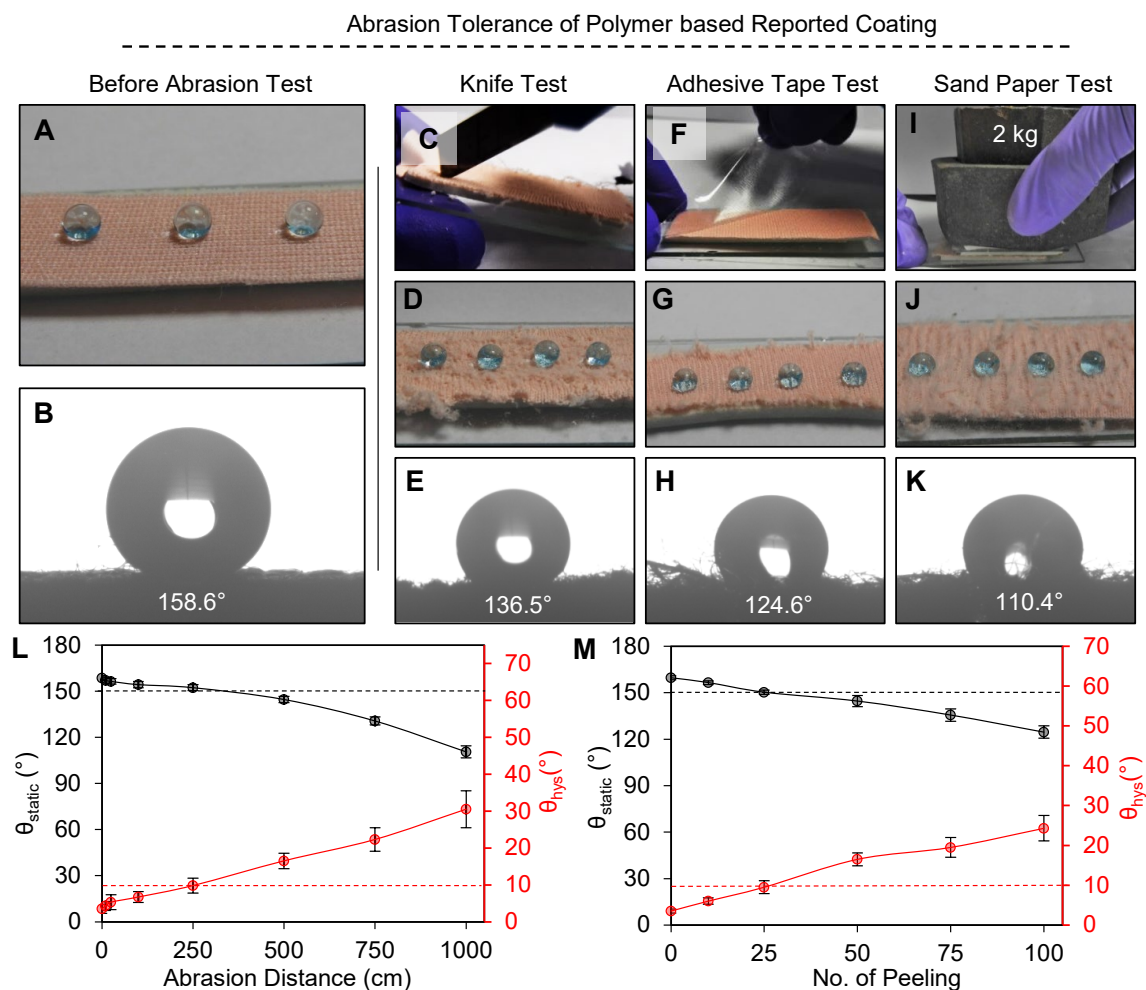


Figure 2.10 A-B) Digital images (A) and contact angle images (B) of beaded water droplet on polymer coated superhydrophobic fabric. C,F,I) Digital images of the experimental setup for knife test (C), adhesive tape peeling test (F), sand paper abrasion test (I). D-K) Digital images(D,G,J) and contact angle images (E, H, K) of the beaded water droplets after performing knife test (D-E), adhesive tape peeling test (G-H) and sand paper abrasion test (J-K) on polymer coated superhydrophobic fabric. L) The plots showing the changes in the static contact angle (black) and respective contact angle hysteresis (red) of beaded water droplet on gradual increment of abrasion distance during the course of sand paper test on polymer coated superhydrophobic fabric. M) The plots illustrating the changes in static contact angle (black) and respective contact angle hysteresis (red) of beaded water droplet on the superhydrophobic interface after repetitive exposure to adhesive tape peeling test on polymer coated superhydrophobic fabric.

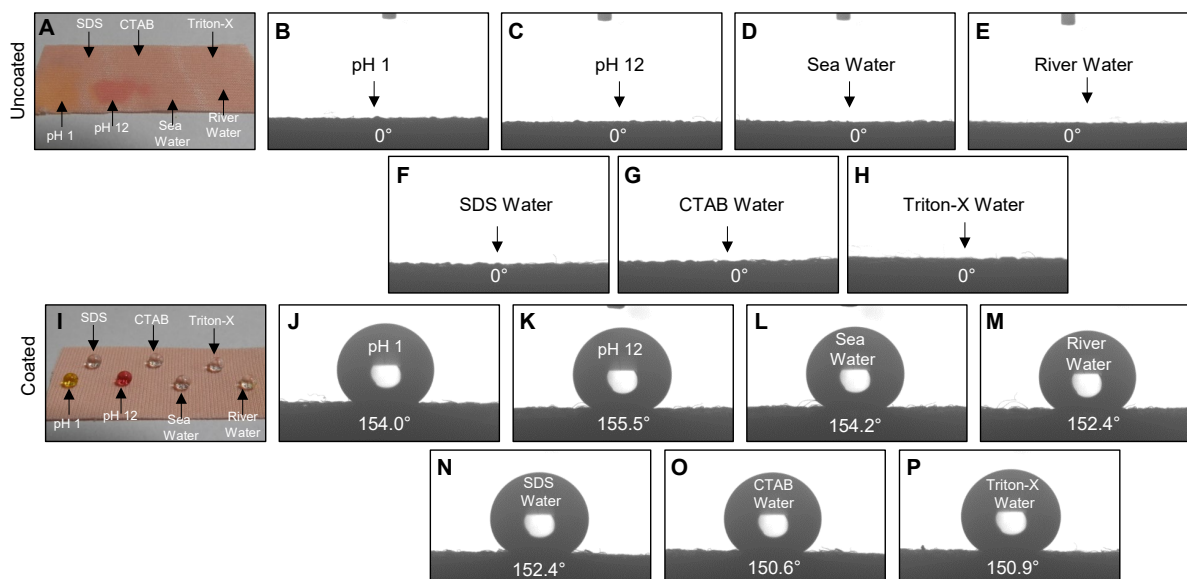


Figure 2.11 Digital images (A, I) and contact angle images (B-H, J-P) of beaded droplets of acidic water (pH 1; B, J), alkaline water (pH 12; C, K), sea water (D, L), river water (E, M) and surfactants (SDS (2mM; F, N), CTAB (2 mM; G, O), Triton-X (2 mM; H, P) added aqueous phase on both the uncoated (A-H) and coated (I-P) fibrous substrates.

abrasion distance (Figure 2.7J). The physically damaged (as evident from Figure 2.7H, I) coated substrate, which was continuously exposed to sandpaper abrasion, displayed extreme water repellency with a static WCA of $\sim 153.2^\circ$. The synthesized superhydrophobic coating remained capable of sustaining a sandpaper abrasion distance of 2250 cm without compromising the embedded extreme water repellence. Further, an increment of the abrasion distance led to the compromise of the non-adhesive superhydrophobicity (Figure 2.7J). Again, the same reaction mixture of small molecules was deposited on a selected fibrous substrate following a dip-coating process to compare the performance of the embedded superhydrophobicity with the spray-

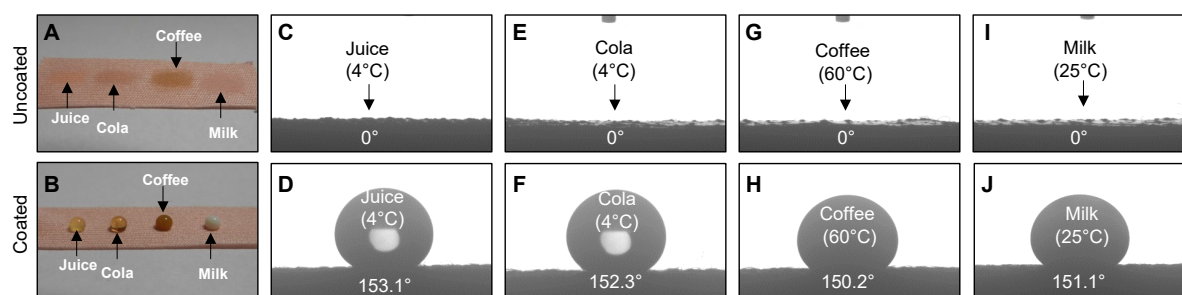


Figure 2.12 Digital images (A-B) and contact angle images (C-J) of beaded droplets of juice (C-D), cola (E-F), coffee (G-H) and milk (I-J) on both the uncoated (A,C,E,G,I) and coated (B,D,F,H,J) fibrous substrate.

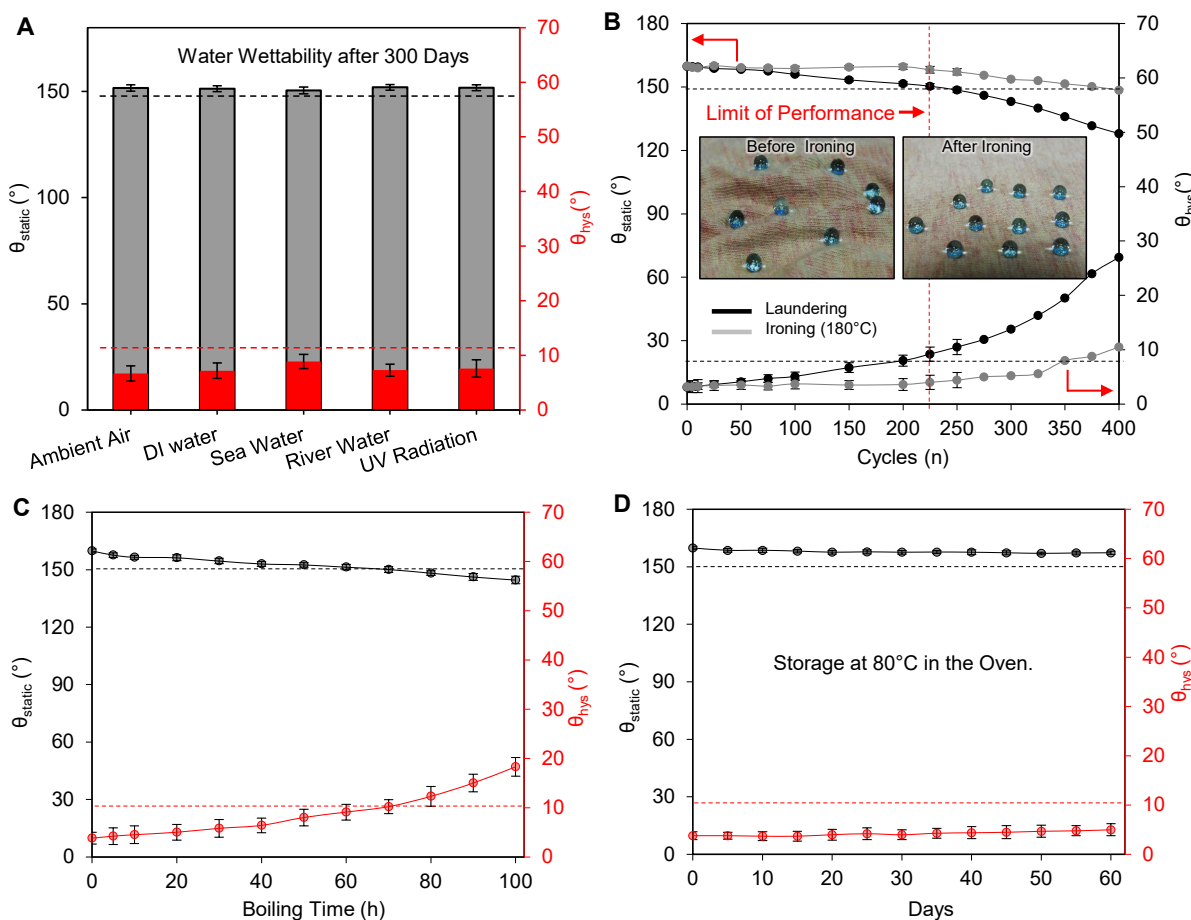


Figure 2.13 A) Plot accounting for the impact of practically relevant various and challenging exposures of ambient (25 °C) air, DI-water, artificial seawater, river water and UV irradiation (at $\lambda_{\text{max}} = 254$ and 365 nm) for 300 days on the synthesized superhydrophobic coating. B) Plot showing the change in static contact angle and contact angle hysteresis of beaded water droplet on the superhydrophobic fabric after conducting repetitive washing (black; the red dotted line indicating the limit of performance, i.e. 250 cycles) and ironing (grey; the blue dotted line referring to the limit of performance, i.e. 375 cycles) test (400 cycles), where the insets are digital images of superhydrophobic coating before and after ironing test. C) The plots showing the changes in static contact angle (black) and respective contact angle hysteresis (red) of beaded water droplet on the synthesized superhydrophobic interface that treated with boiling water for 50 h. D) The plots accounting the changes in static contact angle (black) and respective contact angle hysteresis (red) of beaded water droplet on non-adhesive superhydrophobic coating during its prolonged (30 days) treatment at high temperature (80°C).

deposited coating. The dip-coated interface displayed non-adhesive superhydrophobicity with a WCA of 159° (Figure 2.8). The performance of the dip-coating at challenging abrasive exposure was observed to be very similar to the spray-coating of the same reaction mixture (Figure 2.9). Thus, the process of depositing the reaction mixture has minimal impact on the durability of the

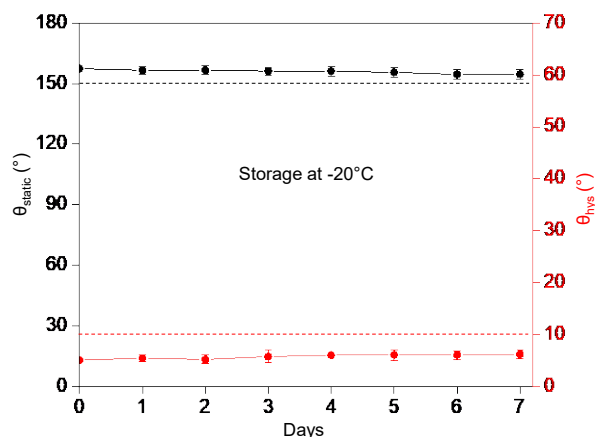


Figure 2.14 The plots accounting for the changes in static contact angle (black) and respective contact angle hysteresis (red) of beaded water droplet on non-adhesive superhydrophobic coating during its exposure at low temperature (-20°C) for 7 days.

embedded superhydrophobicity. Further, the durability of the synthesized coating is compared with an earlier reported polymeric superhydrophobic spray coating²⁶ on the same substrate under identical abrasive conditions. The polymer derived spray coating that was prepared following the reported protocol²⁶ can survive sandpaper abrasion distance of only 250 cm and adhesive tape peeling test only for 25 times under identical experimental conditions, as shown in Figure 2.10. Thus, the small molecules derived coating provided superior and exemplary durability in comparison to the earlier reported polymeric coating, where the selected substrate and abrasive exposures were kept identical for both the small molecules derived coating and earlier reported polymeric coating. The small molecules derived superhydrophobic coating extremely repelled various and relevant chemically complex aqueous phases, as shown in Figures 2.11 and 2.12. The bioinspired extreme water repellence survived prolonged (300 days) exposures to ambient air, DI-water, artificial sea water, river water and UV light, with static WCA above 150° and contact angle hysteresis below 10° , as shown in Figure 2.13A. This exemplary chemical durability of the coating is attributed to the strategic association of robust 1, 4-conjugate addition reaction. The synthesized superhydrophobic coating was also repetitively (400 times) washed with surfactant (SDS) added aqueous phase following a standard and reported procedure. Even after 250 times of washing, the superhydrophobicity remained intact with static WCA above 150° and contact angle hysteresis below 10° as shown in Figure 2.13B. However, the embedded superhydrophobicity was compromised on further repetition of the washing cycle (Figure 2.13B). The synthesized superhydrophobic interface remained repellent to boiling water (Figure 2.13C) and prolonged (30

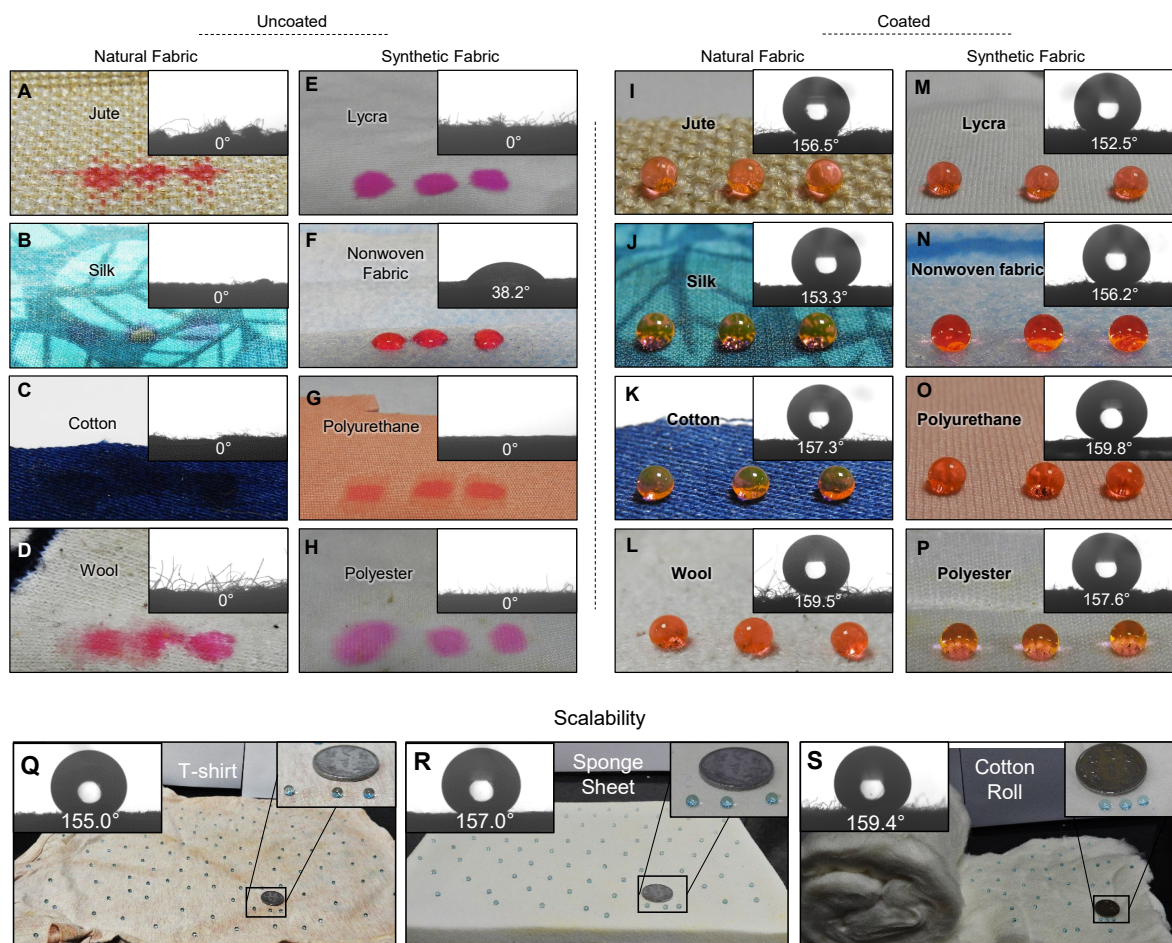


Figure 2.15 A-H) Digital and contact angle images (inset) of beaded water (red color aids visual inspection) droplet on uncoated different natural and synthetic fibrous substrates including jute (A), silk (B), cotton (C), wool (D), lycra (E), nonwoven F), polyurethane (G) and polyester (H) fabric. All the selected substrates are inherently hydrophilic and soaked beaded water droplets. I-P) Digital and static contact angle image (inset) of AEAPTMS@ODAc coated different natural and synthetic fabric including jute (I), silk (J), cotton (K), wool (L), lycra (M), nonwoven fabric (N), polyurethane (O) and polyester (P). Q-S) Digital and static contact angle (inset) image of AEAPTMS@ODAc coated large scale substrate including a T-shirt (Q), melamine sponge (R) and cotton roll (S).

days) exposure to both high (80 °C; Figure 2.13D) and low temperature (-20 °C) for 7 days (Figure 2.14). The bio-inspired coating continued to perform even after ironing the interface at 180 °C for 375 times (Figure 2.13B). During the process of ironing at 180 °C, the creasing marks disappeared from the wrinkled superhydrophobic surface as shown in the inset image of Figure 2.13B. The fluorine-free and small molecules derived, the optically transparent and highly tolerant superhydrophobic coating can be successfully applied on various natural and synthetic hydrophilic substrates (Figure 2.16A-H), including jute fabric, silk fabric, cotton fabric, woolen fabric, lycra

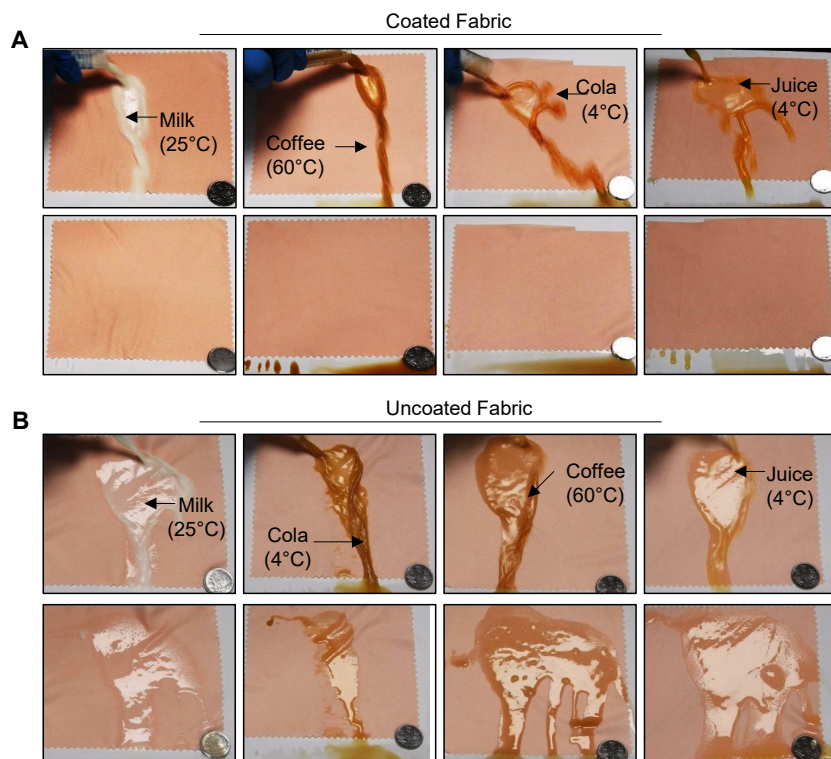


Figure 2.16 A) Digital images depicting the antifouling performance of superhydrophobic coating with the stream of cow milk, hot (60 °C)-coffee, cold (4 °C)-cola and cold (4 °C) juice. B) Digital images depicting the wetting of uncoated fabric with the stream of cow-milk, hot (60 °C)-coffee, cold (4 °C)-cola and cold (4 °C) juice.

fabric, non-woven fabric i.e. commercially available surgical mask, polyurethane fabric and polyester fabric as shown in Figure 2.16I-P. Due to the inherent simplicity of the synthesis process, practically relevant different large objects (e.g. cotton T-shirt, melamine sponge and cotton roll) can also be easily decorated with extreme water repellence as shown in Figure 2.16Q-S.

2.3.3 Demonstrations of Various Outdoor Applications

The embedded superhydrophobic coating prevented the wetting of the coated interface by streams of milk, coffee, cola, and juice as shown in Figure 2.16A, however, the uncoated substrate readily soaked these commercially available common beverages (Figure 2.16B). Next, a hydrophilic T-shirt that decorated with the small molecules derived superhydrophobic coating was examined for self-cleaning performance. Firstly, the coated T-shirt was contaminated with dust and dirt particles before being exposed to the aqueous stream. The physically deposited dust and dirt particles on the coated interface were readily removed and left behind a dry and clean interface (Figure 2.17C, D), whereas similar treatment of the uncoated T-shirt yielded a wet and dirty interface (Figure

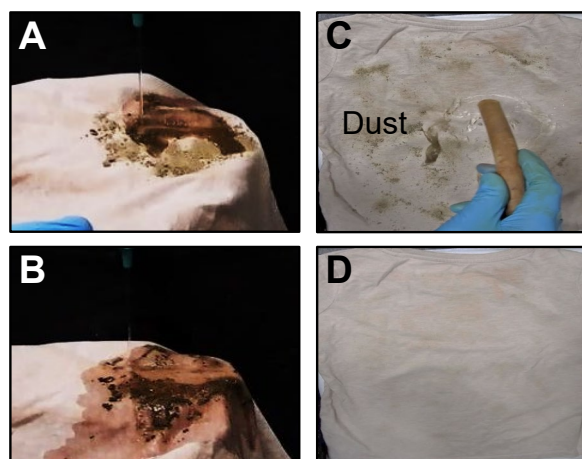


Figure 2.17 A, B) Digital images showing the wet and dirty interface of uncoated t-shirt (A, B) under the exposure of stream of water. C, D) Illustrating the self-cleaning of deposited dust and dirt on the coated (C, D) T-shirt.

2.17A, B). Next, the superhydrophobic fibrous interface was extended as a selective oil-filtrating membrane for performing the gravity-driven and environment-friendly oil/water separation.³⁻⁴ A lab-made porotype was developed, where the superhydrophobic fabric was used as a membrane as shown in Figure 2.18A. Next, oil/water mixtures, which were prepared using either heavy oil

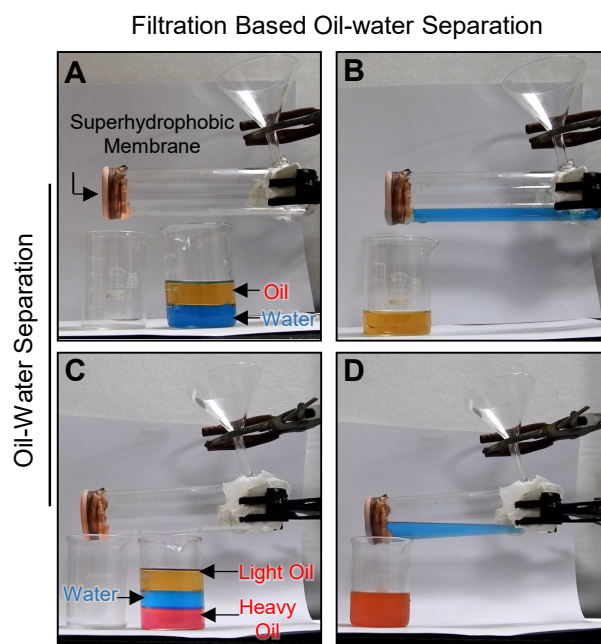


Figure 2.18 A, B) Digital images illustrating the selective collection of light oil (petrol) from the oil–water mixtures, where the superhydrophobic coated fibrous substrate acted as a membrane for selective filtration of oil phase. C, D) Digital images illustrating the separation of three phases (light oil/water/heavy oil) oil–water mixtures using the same superhydrophobic interface.

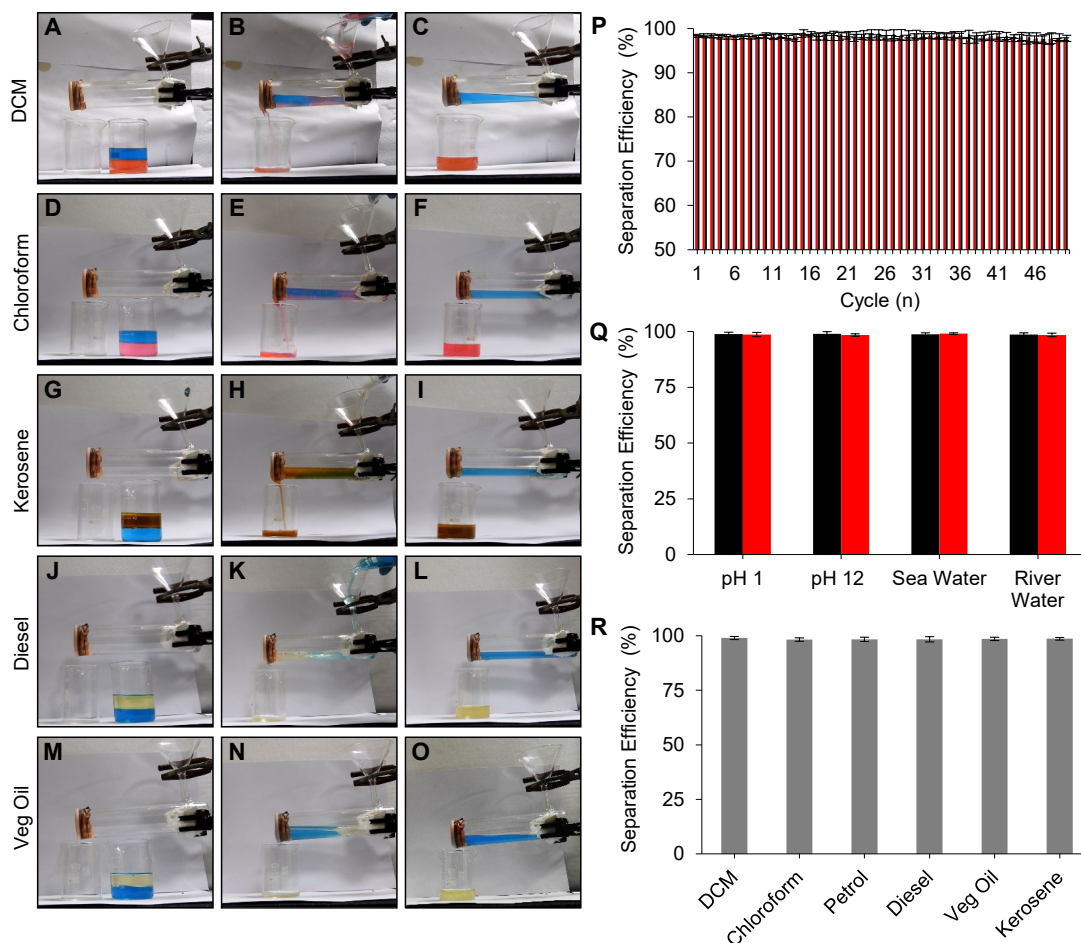


Figure 2.19 A-O) Illustrating the successful separation followed by collection of oil phase from oil/water (coloured with blue dye) mixtures which were prepared using model heavy oils (DCM (A-C), Chloroform (D-F)) and floating oils (kerosene (G-I), diesel (J-L) and veg oil (M-O)). P) Bar graph representing the repetitive (minimum 50 times) collection efficiency of heavy oil (DCM; black) and floating oil (petrol) from its corresponding oil-water mixture, where the superhydrophobic coated fibrous substrate is used as a selective oil filtrating membrane. Q) Graph accounting for the collection efficiency of heavy oil (DCM; black) and light oil (petrol; red) from respective oil/water mixture at various severe harsh conditions including pH 1, pH 12, seawater, and river water. R) Graph accounting for the collection efficiency of different oil/oily phases from corresponding oil-water mixtures.

(Figure 2.19A-F) or light oil (Figure 2.18A-B and Figure 2.19G-O), were successfully separated using the lab-made prototype. The oil phase was selectively filtrated through the superhydrophobic interface. The filtrated oil phase was collected in an individual container that was placed under the prototype (Figure 2.18B, 2.19C, F, I, L, O). Furthermore, a three-phase oil–water mixture (Figure 2.18C) comprising of model heavy oil (DCM, bottom layer), dye added (blue coloured, middle layer) aqueous phase and light oil (diesel, top layer), was also used to demonstrate successful

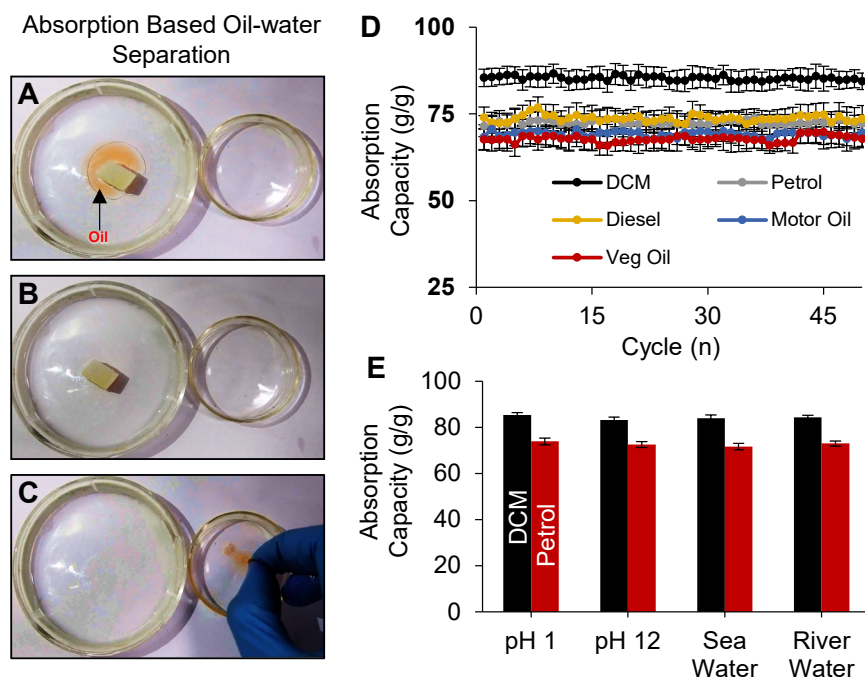


Figure 2.20 A-C) Illustrating selective absorption and collection of the floating oil droplet on aqueous phase by the superhydrophobic melamine sponge. D) Plot representing the repetitive (50 times) absorption capacity for different oil/oily phases including DCM, diesel, veg oil, motor oil, petrol. E) Graph accounting for the absorption capacity of both heavy oil (DCM; black) and light oil (petrol; red) under practically relevant diverse and harsh condition including pH 1, pH 12, sea water, river water.

separation of oil phase from the aqueous phase. Only the oil phases passed through the superhydrophobic interface while the aqueous phase remained incapable of overcoming the superhydrophobic barrier (Figure 2.18D). The oil/water separation performance remained above 98 wt.% for various commonly used fuels (petrol, diesel, kerosene, vegetable oil etc.) and organic solvents (chloroform and DCM) as shown in Figure 2.19R. The same superhydrophobic fabric remained effective in repetitively (50 times) separating the oil-water mixture with high separation efficiency, as shown in Figure 2.19P. Thereafter, this oil/ water separation performance was investigated with both model heavy oil (DCM, black bars) and light oil (petrol, red bars) at practically relevant challenging settings including extremes of pH (1 and 12), artificial seawater and river water (Brahmaputra River, Guwahati). Even in the presence of challenging scenarios, the embedded superhydrophobicity continued to perform with unperturbed efficiency as shown in Figure 2.19Q. Next, the superhydrophobic MF sponge was extended for selective absorption-based oil–water separation and successfully cleaned up from the aqueous phase (Figure 2.20A-C). Further, the application of manual compressive strain led to the recovery of the absorbed oil phase

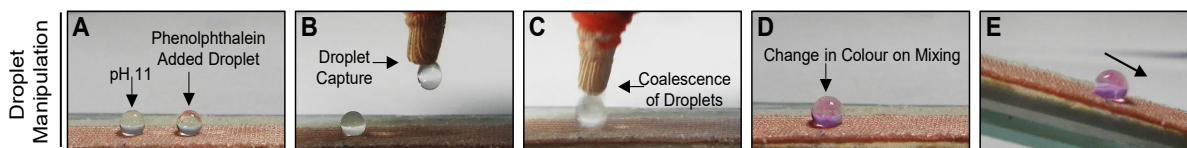


Figure 2.21 A-E) Digital images illustrating the no-loss mixing (B-E) of two beaded aqueous droplets (5 μ L) on non-adhesive superhydrophobic surface by strategic use of an adhesive superhydrophobic coating, where the adhesive superhydrophobicity allowed to capture (B) and coalescence (C) of phenolphthalein added droplet with an alkaline (pH11) aqueous droplet. The mixing of these two droplets lead to a colour change (D), finally the tilting of non-adhesive superhydrophobic interface allowed no-loss transfer (E).

as shown in Figure 2.20C. The same superhydrophobic sponge was repetitively (for 50 times) used for the removal of various oil/oily phases with high absorption capacity (above 65 g/g) as shown in Figure 2.20D. Moreover, the high and selective oil-absorption capacity remained unaffected at practically relevant challenging scenarios—including extremes of pH, seawater and river water as shown in Figure 2.20E.

Thereafter the superhydrophobic coating with tailorable adhesive interaction with the aqueous phase was exploited for controlled, no-loss mixing and transfer of aqueous droplets as shown in Figure 2.21A-E. Such a design of bio-inspired coating is unprecedented in the literature and would be useful for various relevant applications in ‘real-world’ scenarios.

2.4 Conclusions

In summary, a catalyst-free 1,4-conjugate addition reaction between rationally selected small molecules provided a unique deposition solution with prolonged (200 days) shelf-life for achieving durable superhydrophobic coating on various fibrous and porous substrates. The deposition solution can be successfully prepared using various organic solvents and both dip-coating and spray coating approaches can be applied for rapid, single-step and scalable fabrication of extremely water-repellent coating. Further, the concentration of deposition solution and selection of appropriate alkyl acrylate during the 1,4-conjugate addition reaction allowed to modulate both hydrophobicity (from $\sim 134^\circ$ to 160°) and adhesive interaction (from 24 μ N to 204 μ N) between the beaded water droplet and bio-inspired coating, respectively. The synthesized superhydrophobicity remained tolerant to sustain various and severe physical and chemical exposures—including large (150%) and repetitive (2000 cycles) tensile deformation, abrasive sand paper test (with applied pressure: 66 kPa) for 2250 cm distance, repetitive knife scratch test,

adhesive tape peeling test (applied pressure: 66 kPa) for 250 times, exposure to various conditions (artificial sea water, river water, DI water, ambient air) for 300 days, UV irradiation (254 nm and 365 nm) for 300 days, ironing test (180 °C) for 375 times, laundering test for 250 times. Such durable coating achieved following a simple and scalable approach was extended to demonstrate its potential for some relevant and outdoor applications—including self-cleaning, oil/water separation (both selective filtration based and absorption based) and controlled and no-loose manipulation (mixing and transfer) of water droplets. Such an approach would be useful for various other prospective applications in ‘real-world’ conditions.

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Chapter 3: Design of 'Tolerant and Hard' Superhydrophobic Coatings to Freeze Physical Deformation

While the development of mechanically durable and abrasion tolerant superhydrophobicity on rigid substrates itself remains a highly challenging task, the design of superhydrophobic coatings that can restrict both the tensile and compressive deformations of soft and deformable substrates is unprecedented—and such an approach would be of potential interest in various applied and fundamental contexts. In this communication, a reaction mixture was developed following a simple 1,4-conjugate addition reaction between selected small molecules and appropriate cross-linkers for achieving ‘tolerant and hard’ superhydrophobicity—which is not just capable of surviving under severe conditions—but also restricts both the tensile and compressive deformations of the selected soft substrates. The compressive and tensile moduli of the selected soft substrates increased by 2.2×10^4 % and 1.8×10^4 %, respectively, after the deposition of the appropriate reaction mixtures. Moreover, the integration of the cross-linkers in the reaction mixture provided a facile basis to resist the physical erosion/rupture of the selected soft substrates under severe abrasive conditions. Thus, a simple and elegant chemical approach not only controlled the mechanical properties of the porous and fibrous soft substrates under ambient conditions—but also provided highly tolerant superhydrophobicity—which is likely to lead to various outdoor applications.

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3.1 Introduction

Lotus leaves exhibit extreme water repellency with water contact angles (WCAs) above 150°; this property is termed as superhydrophobicity—which emerged as a prospective avenue for developing various functional materials in the recent past.^{1–10} But the durability of such nature-inspired artificial water wettability remains a major concern, thus restricting its widespread, prospective application in outdoor settings.^{11,12} In the last few years, various strategies have been introduced to develop abrasion tolerant and mechanically durable superhydrophobic coatings.^{13–18} Although some of these seminal reports succeeded in achieving durable superhydrophobic coatings on rigid substrates, most of the reported approaches followed either complex fabrication processes or required sophisticated instrumental set-ups.^{13–19} Moreover, the previously reported durable superhydrophobic coating approaches lacked the ability to tailor the mechanical properties of the soft and geometrically complex (fibrous and porous) substrates.^{13–19} Moreover, most of the reported durable superhydrophobic coatings were mostly derived using fluorinated components—which are likely to pose environmental hazards.^{13–19} In contrast to the earlier approaches, this current communication introduced a fluorine free and facile design—for developing a tolerant and hard coating on selected soft and geometrically complex objects—with customized mechanical properties.

Superhydrophobic coatings on inherently soft fibrous and/ or spongy substrates have shown immense potential for widespread application—including oil–water separation, smart strain sensors, temperature and pressure sensing, anti-blood repellence, etc.^{4–8} Recently, a few approaches were introduced to prepare non-compressible superhydrophobic monoliths/ concrete, which could be beneficial for developing smart architectures, ships, aircraft, etc.^{1,9,10} Thus, the design of both deformable and non-deformable superhydrophobic materials/interfaces are of potential interest for various relevant applications. Earlier, numerous distinct and multistep approaches were adopted to prepare non-deformable monoliths, compressible sponges and stretchable superhydrophobic interfaces.^{1,4–10} Interestingly, the design of a common and single step fabrication process to prepare two distinct and tolerant superhydrophobic coatings that would either allow or restrict the physical deformation of the underlying highly compressible and stretchable substrates is yet to be introduced in the literature.

In the past, different nanomaterials and microparticles were commonly and widely explored for tailoring the mechanical properties of synthesized materials.^{20–24} In contrast to such conventional approaches, in this communication, we report a facile 1,4-conjugate addition reaction under ambient conditions between selected reactants, i.e. [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS) and octadecyl acrylate (ODAc), in the presence and absence of cross-linker molecules [pentaerythritol triacrylate (3-Acl) or dipentaerythritol penta-acrylate (5-Acl)] to develop either non-deformable or deformable (compressible/stretchable) superhydrophobic coatings on selected soft and deformable underlying

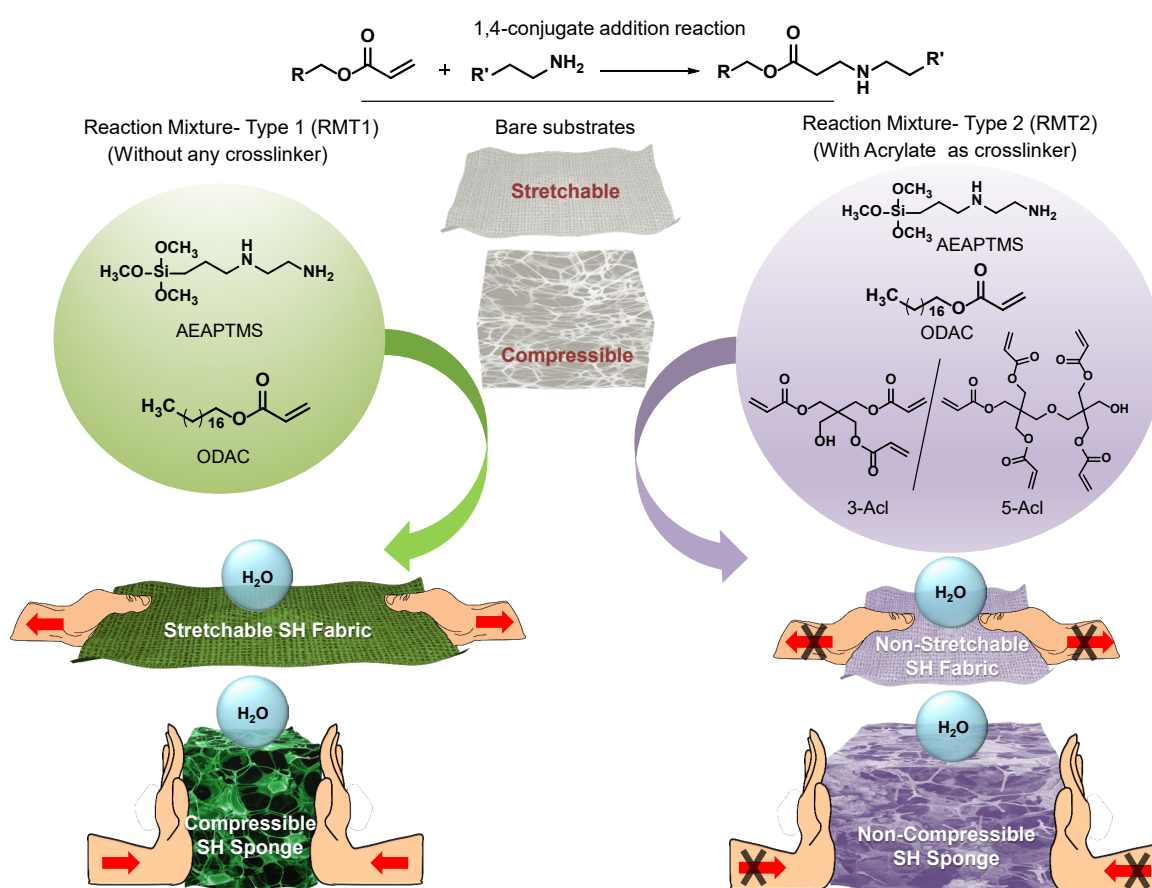


Figure 3.1 A schematic illustration for the preparation of deformable and non-deformable superhydrophobic materials following 1,4-conjugate addition reaction between acrylate and amine functional groups via a simple dip-coating method. Reaction between two small molecules [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS) and octadecyl acrylate (ODAc) produced stretchable and compressible superhydrophobic materials, whereas the incorporation of selected crosslinker molecules (either pentaerythritol triacrylate (3-Acl) or dipentaerythritol penta-acrylate (5-Acl)) in the reaction mixtures of AEAPTMS and ODAc resulted in the formation of non-stretchable, non-compressible, tolerant, and hard superhydrophobic materials.

substrates, i.e., polyurethane fabric (highly stretchable) and melamine formaldehyde sponge, respectively, as shown in Figure 3.1. The reaction mixture comprised of the selected cross-linker as other small molecules based reactants successfully restricted the physical deformation of the used soft and highly deformable substrates while displaying exemplary tolerance to severe abrasions and high external impact, without compromising the embedded superhydrophobicity. In fact, the covalent crosslinking chemistry significantly suppressed (12% with 5-Acl vs 80% without 5-Acl) the physical erosion of the selected melamine formaldehyde sponge in extremely abrasive settings.

3.2 Experimental Section

3.2.1 Materials Required

Pentaerythritol triacrylate (3-Acl; molecular weight: 298.29 g/mol), dipentaerythritol pentaacrylate (5-Acl; molecular weight: 524.51 g/mol) were obtained from Sigma Aldrich (Bangalore, India). Details of other chemicals used in this work are given in Chapter 2.

3.2.2 Characterization

Mechanical properties were measured using 5 kN Electromechanical Universal Testing Machine. Details of other characterization techniques used in this work are given in Chapter 2.

3.2.3 Fabrication of Robust Superhydrophobic Coating

Both melamine formaldehyde foam and polyurethane fabric were washed with acetone before applying dip coating. Mainly two distinct types of reaction mixtures (RM) were prepared with and without using crosslinkers. The reaction mixture prepared by mixing 6 mL of 3-(2-aminoethylamino)propyl] trimethoxysilane (AEAPTMS) and 9 g of octadecyl acrylate (ODAc) in 24 mL of ethanol, was termed as RMT1. Next polyurethane fabric and melamine foam were dipped in the RMT1 and kept for 10 min under agitation followed by drying in oven at 70 °C to obtain the superhydrophobicity. Another reaction mixture was prepared by mixing 6 mL of [3-(2-aminoethylamino)propyl] trimethoxysilane (AEAPTMS), 3.12 g octadecyl acrylate (ODAc) and 1.78 g pentaerythritol triacrylate (3-Acl) in 24 ml of ethanol, which was denoted as RMT2A. Similarly, another reaction mixture prepared by mixing 6 mL of [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS), 3.12 g of octadecyl acrylate (ODAc) and

1.88 g of dipentaerythritol penta-acrylate (5-Acl) in 24 mL of ethanol, was termed as RMT2B. The same fabrication procedure mentioned for RMT1 coated materials was followed to prepare the RMT2A and RMT2B coated substrates.

3.2.4 Tailoring Mechanical Property of Superhydrophobic Material

Reaction mixture of RMT2B comprises of three reactants [3-(2-Aminoethylamino)propyl] trimethoxysilane (AEAPTMS), octadecyl acrylate (ODAc) and dipentaerythritol penta-acrylate (5-Acl). To demonstrate tailored mechanical property, a series of reaction mixtures has been prepared where 5-Acl concentration have been varied from 0 mM to 140 mM—keeping the ratio of acrylate group to primary amine group identical (1:1). In these series of reaction mixtures, the amount of AEAPTMS remained unaltered—but the concentrations of 5-Acl and ODAc changed. Hence, the increase in the concentration of 5-Acl in the reaction mixture of RMT2B, reduced the concentration of ODAc to maintain the acrylate to amine functional groups as 1:1. The superhydrophobic coating with tailored mechanical property was achieved by dipping the selected soft substrate in the respective reaction mixture for 10 minutes. On increasing the concentration of 5-Acl in RMT2B, the mechanical property has been gradually improved. Details of reactant amounts in different reaction solutions are given in Table 3.1.

Concentration of 5-Acl (mM)	Amount of 5-Acl (g)	Amount of ODAc (g)	Amount of AEAPTMS (mL)
0	-	9	6
20	0.31	7.98	6
40	0.62	7.01	6
60	0.94	6.03	6
80	1.25	5.06	6
100	1.57	4.09	6
120	1.88	3.11	6
140	2.21	2.14	6

Table 3.1 Accounting for the detailed formulation of the reaction mixture that provided superhydrophobic coating with tailored mechanical properties.

3.2.5 Mechanical Performance of the Prepared Coatings

Mechanical properties of the synthesized superhydrophobic materials were determined using 5 kN Electromechanical Universal Testing Machine. For measuring the compressive strength, both bare

and coated (RMT1, RMT2A and RMT2B) melamine foams were cut with the dimension of 4 cm $\times$ 2.5 cm $\times$ 2.5 cm. For tensile strength measurement, bare and coated (RMT1, RMT2A and RMT2B) polyurethane fabric of dimension 5 cm $\times$ 2 cm was used. All the experiments were performed under ambient conditions.

3.2.6 Physical and Chemical Durability

Different physical and chemical durability tests were performed on both superhydrophobic melamine foam and polyurethane fabric. Detailed procedures for all the durability tests were explained in the section given below.

3.2.6.1 Sand Paper Abrasion Test

A 400-grit abrasive sandpaper (2 cm radius) was rubbed manually in a back-and-forth direction across the superhydrophobic melamine foam of area 2 cm $\times$ 1 cm with an applied pressure of 25 kPa for about a distance of 250 cm. The same sandpaper abrasion test was carried out for superhydrophobic polyurethane fabric. The fabric (7 cm $\times$ 2 cm) was rubbed with sandpaper of size 3 cm $\times$ 3 cm $\times$ 1 cm in backward and forward directions for 3000 cm distance with an applied pressure of 25 kPa. Afterwards, the anti-wetting property of both melamine foam and polyurethane fabric was monitored by measuring the contact angle of water droplet. Coloured water droplets were placed on the abraded area of both substrates for visual inspection of water wettability.

3.2.6.2 Knife Scratch Test

Both superhydrophobic melamine foam and polyurethane fabric were scratched manually with a sharp knife multiple times in different directions randomly. Then wettability of both substrates was checked by placing coloured water droplets on the scratched area of the substrates and by measuring the contact angle.

3.2.6.3 Adhesive Tape Peeling Test

An adhesive tape was attached to the surface of superhydrophobic melamine foam and polyurethane fabric with an applied load of 500 g to ensure proper contact between the surface and adhesive tape surface. Then the adhesive tape was removed manually from the surface of the material. This procedure was repeated for 250 times. Thereafter, the water wettability was inspected through visual inspection and contact angle measurement.

3.2.6.4 Chemical Durability Test

To test the chemical durability, superhydrophobic melamine foam and polyurethane fabric were exposed separately to diverse chemically harsh aqueous media such as extremes of pH (pH 1 and pH 12), artificial seawater (solution of 0.226 g MgCl_2 , 0.325 g MgSO_4 , 2.673 g NaCl , and 0.112 g CaCl_2 in 100 mL of deionized water), river water (Brahmaputra, Assam, India) surfactants contaminated water (1 mM sodium dodecyl sulphate (SDS) and 1 mM (1-dodecyl)trimethylammonium bromide (DTAB), triton-X) for 30 days. The impact of these harsh chemicals on the anti-wetting property of the substrates was measured through contact angle measurement and visual inspection.

3.2.6.5 Laundering Test

The washing durability was done following a standard procedure (AATCC Test Method 61-2006 Test No 2A) where the superhydrophobic fabric was washed at 40 °C for 45 min in the presence of 0.37 wt% SDS surfactant. This procedure was repeated for 250 times.

3.3 Results and Discussion

3.3.1 Development of Covalently Cross-Linked Polymeric Gel

In the past, the 1,4-conjugate addition reaction has been instrumental in developing various functional molecules/ materials.^{25–29} Recent reports explored the mutual covalent reaction between amine and acrylate groups under ambient conditions to prepare chemically reactive polymeric nano-complexes—and their strategic deposition allowed to preparing functional and chemically reactive polymeric coatings for optimizing different bio-inspired liquids (oil and water) wettability.^{30,31} However, such polymeric nano-complexes based approaches that commonly depended on multistep fabrication processes failed to restrict the physical deformations (stretching/compression) of the highly deformable selected substrates against the applied stress.^{30,31} In the current design, two distinct small molecules and appropriate cross-linkers were strategically deployed to prepare two types of reaction mixtures: reaction mixture type 1 (RMT1, comprised of AEAPTMS and ODAc) and reaction mixture type 2 [RMT2: comprised of AEAPTMS and ODAc and the selected cross-linker (3-Acl or 5-Acl)]. The physical states of these two types of reaction mixtures were observed to be completely different after mixing the selected reactants under ambient conditions. While RMT1 remained a liquid even after 12 h of mixing of

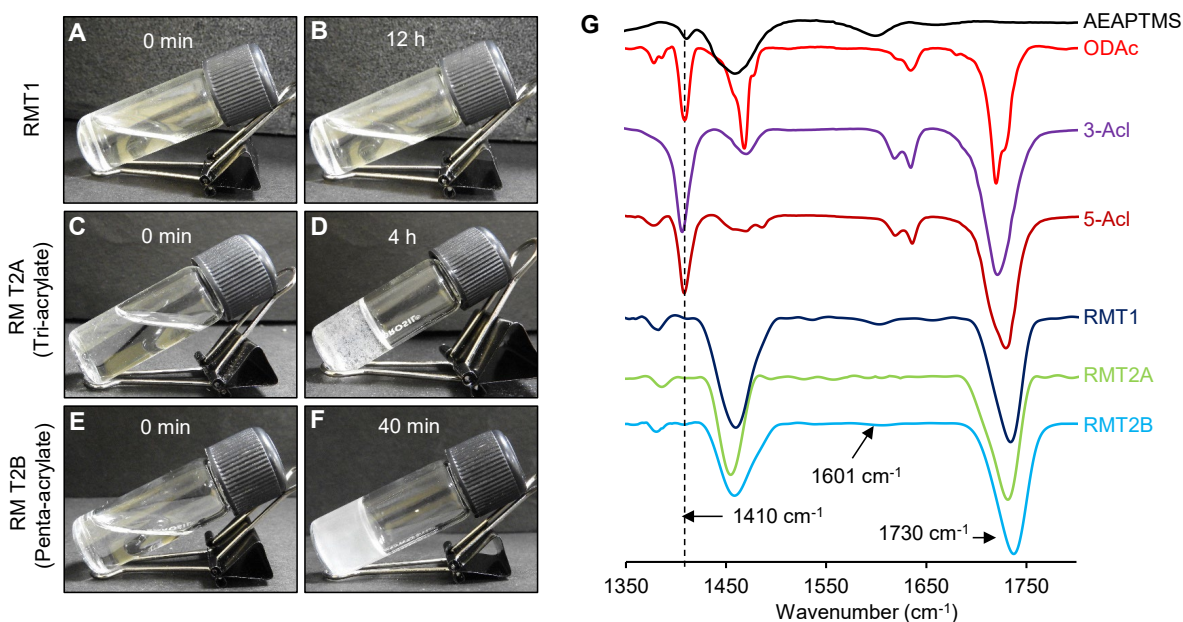


Figure 3.2 A-F) Digital images illustrating the gelation ability of the prepared reaction mixtures in the absence (RMT1; A and B) and in the presence of cross-linkers (RMT2A and RMT2B; C–F). RMT1 did not form a gel even after keeping the reaction solution for 12 h (A and B), whereas RMT2A having pentaerythritol triacrylate (3-Acl) as the cross-linker molecule (C and D) and RMT2B containing dipentaerythritol penta-acrylate (5-Acl) as the cross-linker (E and F) formed gels after 4 h and 40 min respectively. G) FTIR-ATR spectra for the selected reactants [3-(2-aminoethylamino)propyl] trimethoxysilane (AEAPTMS, pink), octadecyl acrylate (ODAc, yellow), pentaerythritol triacrylate (3-Acl, purple) and dipentaerythritol penta-acrylate (5-Acl, red). Further FTIR-ATR spectra for the three different reaction mixtures: RMT1 (blue), RMT2A (green) and RMT2B (black) were recorded. The IR peaks at 1410 cm^{-1} , 1601 cm^{-1} and 1730 cm^{-1} correspond to the C–H deformation of the β -carbon of the vinyl group, the N–H bending of the primary amine group and the C=O group stretching respectively.

AEAPTMS and ODAc, RMT2 (A/B) comprised of different cross-linkers (3-Acl/5-Acl) formed a gel, as shown in Figure 3.2A–F. The reaction mixture having the additional small molecule 3-Acl (denoted RMT2A), which serves as a cross-linker, transformed into a gel after 4 h, as shown in Figure 3.2C and D. However, the use of the other cross-linker, i.e., 5-Acl (labelled RMT2B) instead of 3-Acl, accelerated the gelation process and led to the transformation of the optically transparent reaction mixture (RMT2B) into an opaque gel within 40 minutes as shown in Figure 3.2E and F. The progress of the 1, 4-conjugate addition reaction in all three different reaction mixtures (RMT1, RMT2A and RMT2B) was monitored using attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR). The vinyl moieties of the acrylate groups of the selected reactants (ODAc and 3-Acl/5-Acl) were readily consumed on mutual reaction with the

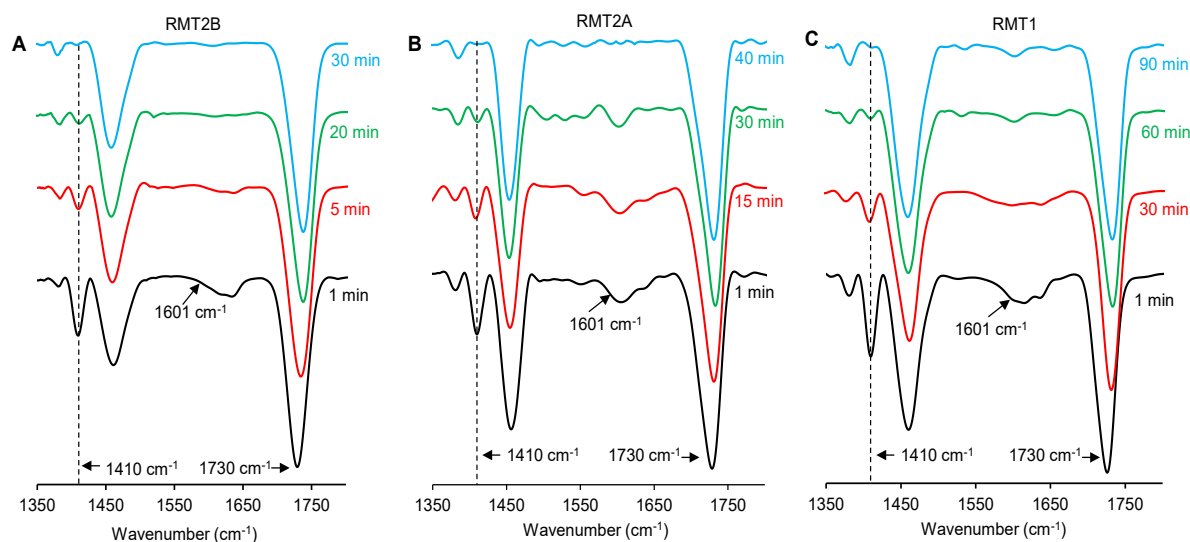


Figure 3.3 A-C) FTIR-ATR spectra of different reaction mixtures- RMT2B (A), RMT2A (B) and RMT1 (C) at regular time intervals with progression of the reaction time.

primary amine of AEAPTMS in the prepared reaction mixtures (RMT1, RMT2A and RMT2B), which was evident from the drastic decrease in the characteristic IR signature of the C–H deformation of the vinyl moiety at 1410 cm^{-1} with respect to the internal standard, i.e. the IR peak for carbonyl stretching at 1730 cm^{-1} as shown in Figure 3.2G. Simultaneously, the characteristic IR bending signature of primary amines at 1601 cm^{-1} corresponding to AEAPTMS completely disappeared after the mutual reaction with acrylate groups. Further, a rapid decrease in the IR signature for the vinyl group in RMT2B was observed, where $\sim 81\%$ of the acrylate groups were consumed in the initial 5 minutes. After 30 minutes, hardly any IR signature for the vinyl moiety was noted as shown in Figure 3.3A. However, a gradual progress of the 1, 4-conjugate addition reaction in both RMT1 and RMT2A reaction mixtures was examined through IR spectral analysis as depicted in Figure 3.3B and C, where the time taken to completely deplete the IR signal for vinyl moiety is longer, in comparison to RMT2B. This study suggested a slower mutual reaction between amine and acrylate groups.

3.3.2 Wettability Characterization of Polymeric Gel Derived Bio-Inspired Coating on Fibrous and Porous Substrates

Subsequently, the three different reaction mixtures (RMT1, RMT2A and RMT2B) were individually deposited on the selected stretchable fabric (polyurethane based) and compressible sponge (melamine formaldehyde). All three reaction mixtures that provided respective coatings

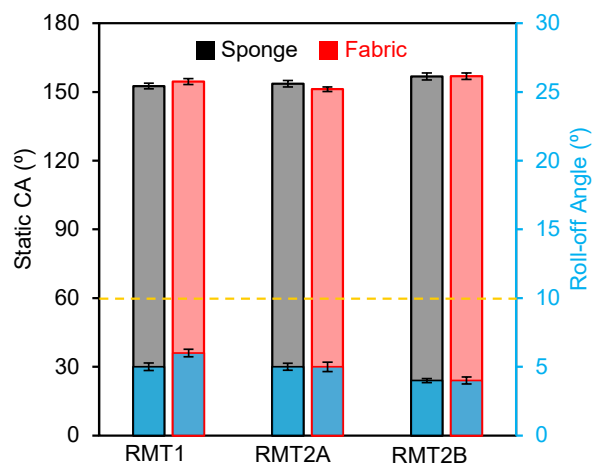


Figure 3.4 Bar plot demonstrating the static contact angles and roll-off angles of materials (melamine sponge, black; polyurethane fabric, red) coated with three reaction mixtures – RMT1, RMT2A and RMT2B.

were efficient in displaying the desired superhydrophobicity with static water contact angles (WCAs) above 150° and roll-off angles below 10° as shown in Figure 3.4. Further, the coated interfaces were efficient in bouncing off an incident stream of an aqueous phase as demonstrated in Figure 3.5A–F. In addition, all the coated substrates displayed a shiny interface underwater (Figure 3.5I–N)—due to the presence of external trapped air—that conferred heterogeneous wettability. Further, the bouncing of water droplet (20 μ l) was noticed on the prepared coatings that were derived from RMT2B (Figure 3.6A, B,) and such interfaces were efficient in self-cleaning the deposited dust and dirt (Figure 3.7A–C). Thereafter, the prepared coating successfully repelled a water jet (Figure 3.8A–C) over a wide range of incident angles (5°, 15°, 45°, 60°). The embedded superhydrophobic coating successfully endured a water jet with a speed of 21 ms^{-1} (the corresponding Weber number is 15000). However, the survival of the superhydrophobic coating beyond the water jet speed of 21 ms^{-1} is not examined in the current study. The Cassie–Baxter equation (eqn (3.1) and (3.2)) was applied to calculate the fraction of contact area (f_i)²⁹ between the beaded water droplet and the respective coated interface.

$$\cos\theta_r = f_1\cos\theta - f_2 \quad (3.1)$$

$$f_1 + f_2 = 1 \quad (3.2)$$

where θ and θ_r are the contact angles on the coated (that were individually derived from RMT1, RMT2A and RMT2B) glass (smooth surface) and porous/fibrous substrates respectively. The fraction of contact area between the coated substrates (i.e. fabric /sponge) and beaded water droplet

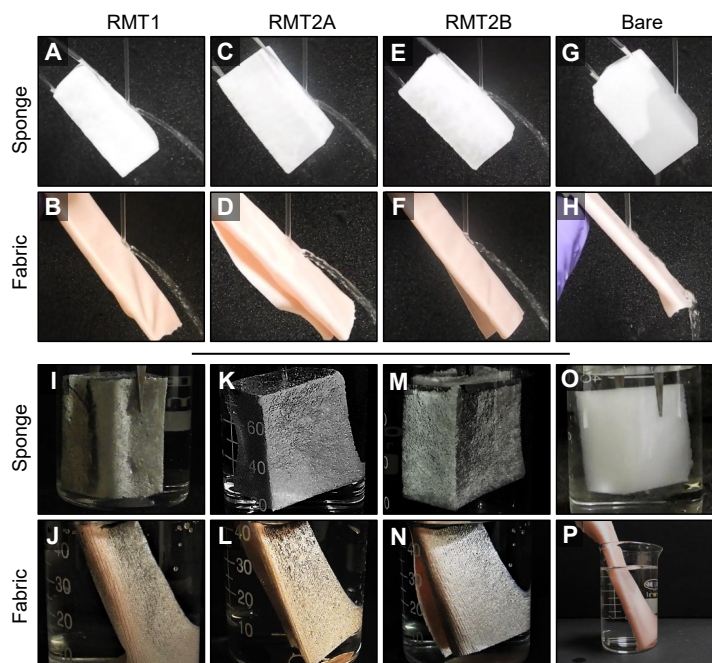


Figure 3.5 A-H) Digital images showing the impact of stream of water after hitting the substrates (melamine formaldehyde sponge and polyurethane fabric) coated with reaction mixtures- RMT1 (A-B), RMT2A (C-D), RMT2B (E-F) and bare substrates (G-H). Water jet readily bounced away upon hitting the coated (RMT1, RMT2A and RMT2B) substrates whereas the bare substrates are completely wetted. I-P) Digital images of substrates (melamine formaldehyde sponge and polyurethane fabric) coated with three different reaction mixtures- RMT1 (I-J), RMT2A (K-L), RMT2B (M-N) and bare substrates (O-P) on submerging under water. Appearance of shiny interface under water for all the substrates coated with these three different reaction mixtures revealed the presence of metastable trapped air whereas the bare substrates become completely wetted upon submerging under water.

is denoted as f_1 , and f_2 refers to the fraction of contact area between the trapped air and beaded water droplet.

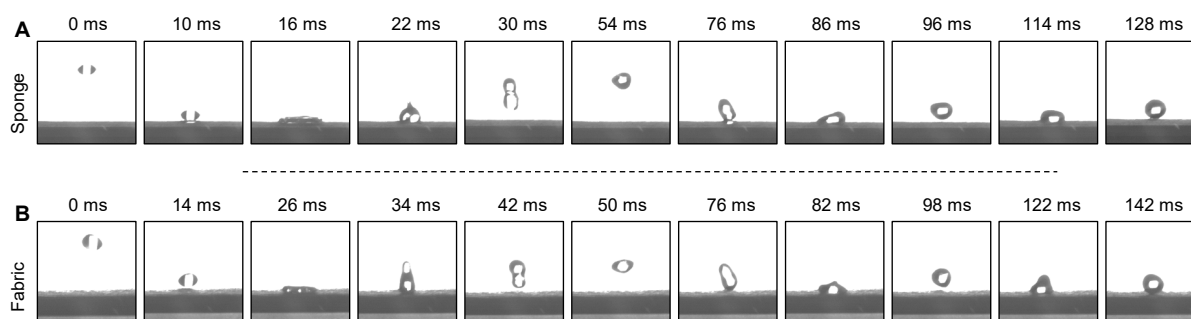


Figure 3.6 A-B) Images captured with high speed camera to demonstrate the impact and bouncing behavior of water droplet (20 μ L, dropped from 25 cm distance) on RMT2B coated superhydrophobic sponge (A) and fabric (B).

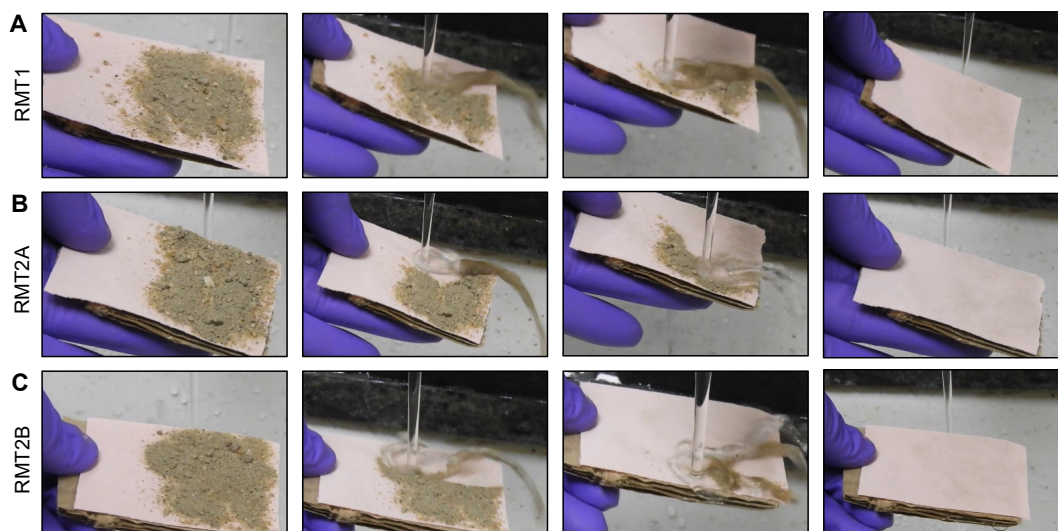


Figure 3.7 A-C) Digital images depicting the self-cleaning performance of deposited dust and dirt particles on RMT1 (A), RMT2A (B) and RMT2B (C) coated superhydrophobic fabrics.

The meta-stable trapped air minimized the fraction (f_l) of contact area between the beaded water droplet and coated surface to 0.092 for both the RMT2B coated sponge and fabric, respectively. Very similar results were obtained for the coatings derived from RMT2A and RMT1 as shown in Figure 3.9A and B. Most of the portion of the beaded water droplet remained in contact with the trapped air phase in the coated interface as depicted in Figure 3.9A and B. After the deposition of each reaction mixture on the porous sponge and fibrous fabric, all the coatings were investigated

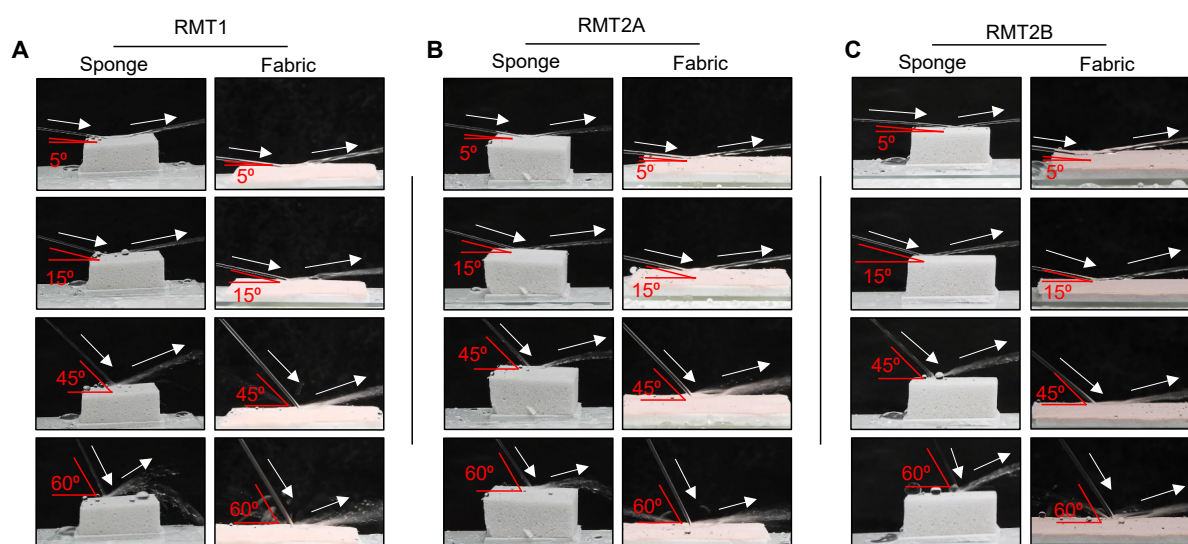


Figure 3.8 A-C) Digital images of water jet that bounced off on RMT1 coated sponge and fabric (A), RMT2A coated sponge and fabric (B), RMT2B coated sponge and fabric (C) over a wide range of incident angles (5°, 15°, 45°, 60°).

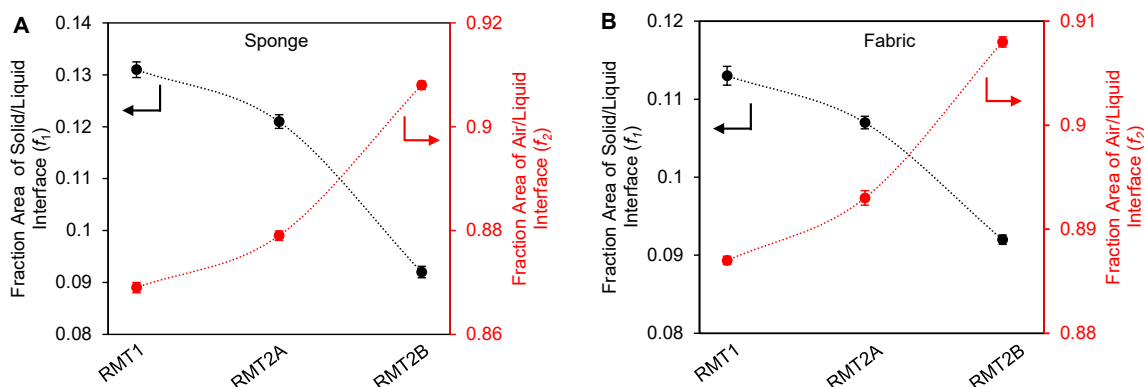


Figure 3.9 A, B) Graph showing the fraction of contact area of solid/ water interface (f_1) and air/water interface (f_2) for melamine formaldehyde sponge (A) and polyurethane fabric (B) coated with three different reaction mixtures- RMT1, RMT2A and RMT2B.

with field emission scanning electron microscope (FESEM) images (Figure 3.10A-H), where the appearance of random rough features (Figure 3.10C–H) on the selected substrates suggested the deposition of the respective reaction mixtures. Again, energy dispersive X-ray (EDX) analysis supported the uniform deposition of respective reaction mixtures on the selected fibrous substrates, as demonstrated in Figure 3.11A–C. It is worth mentioning that ODAc in both the reaction mixtures (RMT1 and RMT2B) played a crucial role in achieving the essential chemical optimization, which conferred superhydrophobicity. The lower analogues [i.e., lauryl acrylate (LAc) and hexyl acrylate (HAc)] of ODAc failed to provide extremely water-repellent interfaces as shown in Figure 3.12I–X, where the WCA remained well below the threshold contact angle—

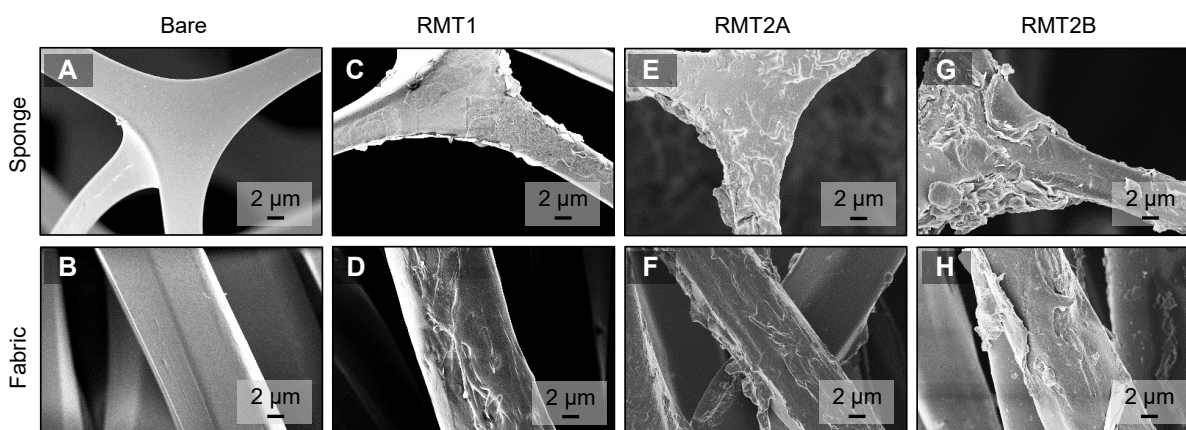


Figure 3.10 A-H) FESEM images of (A and B) bare substrates (sponge, A; fabric, B) and (C–H) substrates coated with the three different reaction mixture solutions RMT1 (sponge, C; fabric, D), RMT2A (sponge, E; fabric, F) and RMT2B (sponge, G; fabric, H).

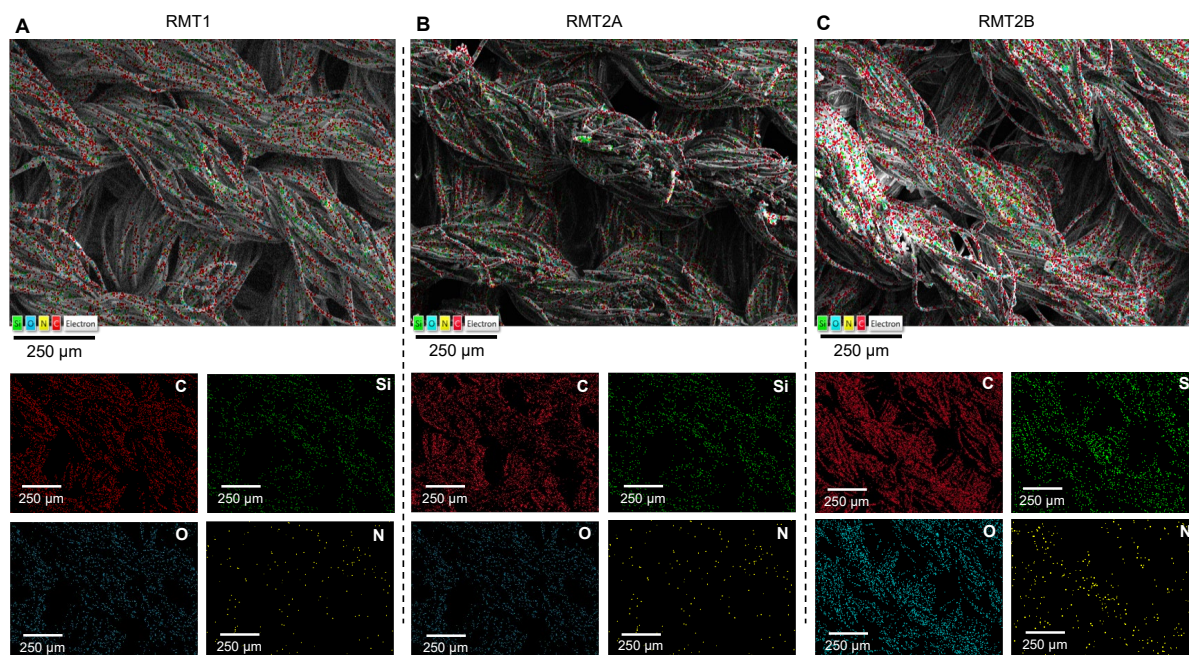


Figure 3.11 A-C) Energy-dispersive X-ray spectroscopy (EDX) images for polyurethane fabric coated with three reaction mixtures – RMT1 (A), RMT2A (B) and RMT2B (C).

i.e., 150° . Thus, the reaction mixtures with appropriately selected reactants are essential for the chemical and physical co-optimization to achieve the desired superhydrophobicity.

3.3.3 Customization of Mechanical Property of Highly Deformable and Stretchable Substrates

Thereafter, the selected stretchable bare fibrous substrate and compressible soft substrate that were successfully coated with distinct types of reaction mixtures, i.e., RMT1, RMT2A and RMT2B, were exposed to external tensile (2 kg load) and compressive (4.3 kg load) stress, respectively, to examine the impact of all organic ingredient based bio-inspired coatings on the mechanical properties of the selected easily deformable substrates. On application of an external load of 4.3 kg on both the bare and RMT1 coated melamine formaldehyde sponges, a highly compressed state of the coated substrate was noted as shown in Figure 3.13A, B, E and F. However, the same spongy substrate coated with RMT2A and RMT2B could tolerate the applied load of 4.3 kg—without causing any deformation as shown in Figure 3.13I, J, M and N. On the other hand, a very similar results were observed for the stretchable fibrous substrate. The stretchable fibrous substrate that underwent 208% tensile strain on the application of a 2 kg external load (Figure 3.13C, D) remained stretchable up to 68% after the deposition of RMT1 as shown in Figure 3.13 G, H.

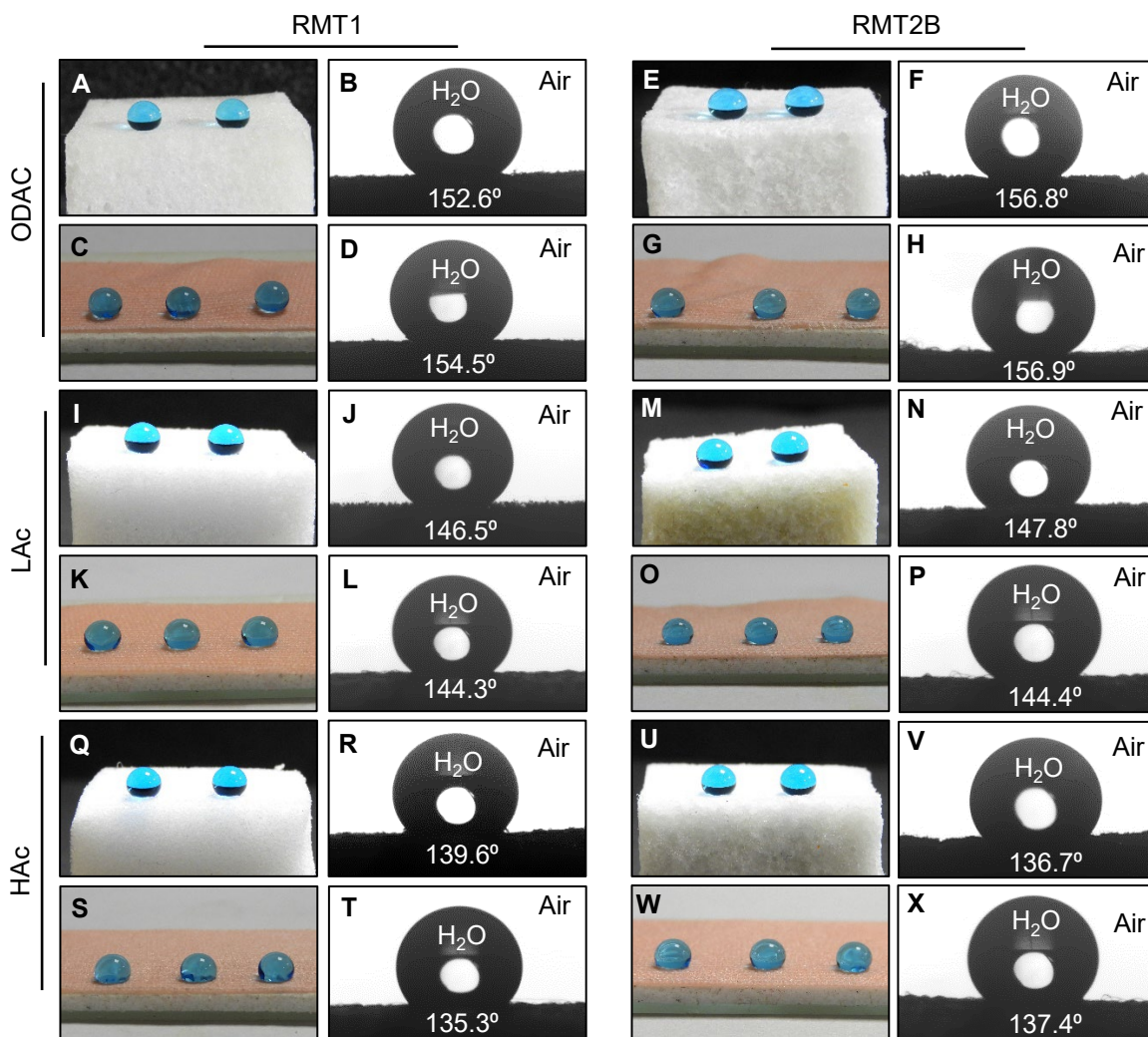


Figure 3.12 Digital images (A, C, E, G, I, K, M, O, Q, S, U and W) and contact angle images (B, D, F, H, J, L, N, P, R, T, V and X) for the substrates (melamine formaldehyde sponge and polyurethane fabric) coated with two different reaction mixtures RMT1 and RMT2B where hydrophobic acrylate moiety in the reaction mixtures has been varied from ODAC (A-H) to its two lower analogues acrylates i.e., LAC (I-P) and HAc (Q-X).

However, a minimal (8%) tensile deformation was observed for the same stretchable fibrous substrate coated with RMT2B as shown in Figure 3.13O, P, whereas 35 % tensile deformation for RMT2A coated stretchable fibrous substrate was noted (Figure 3.13K, L). Further, the compressive modulus of the melamine formaldehyde sponge was estimated before and after the individual dip-coating in the selected reaction mixtures—RMT1, RMT2A and RMT2B. The compressive modulus of the native sponge (0.06 MPa) was increased by ~12 times (0.75 MPa) after depositing RMT1, whereas the compressive modulus of the same substrate was enhanced by ~145 times (9.16 MPa) and ~223 times (14.08 MPa) after the deposition of RMT2A and RMT2B,

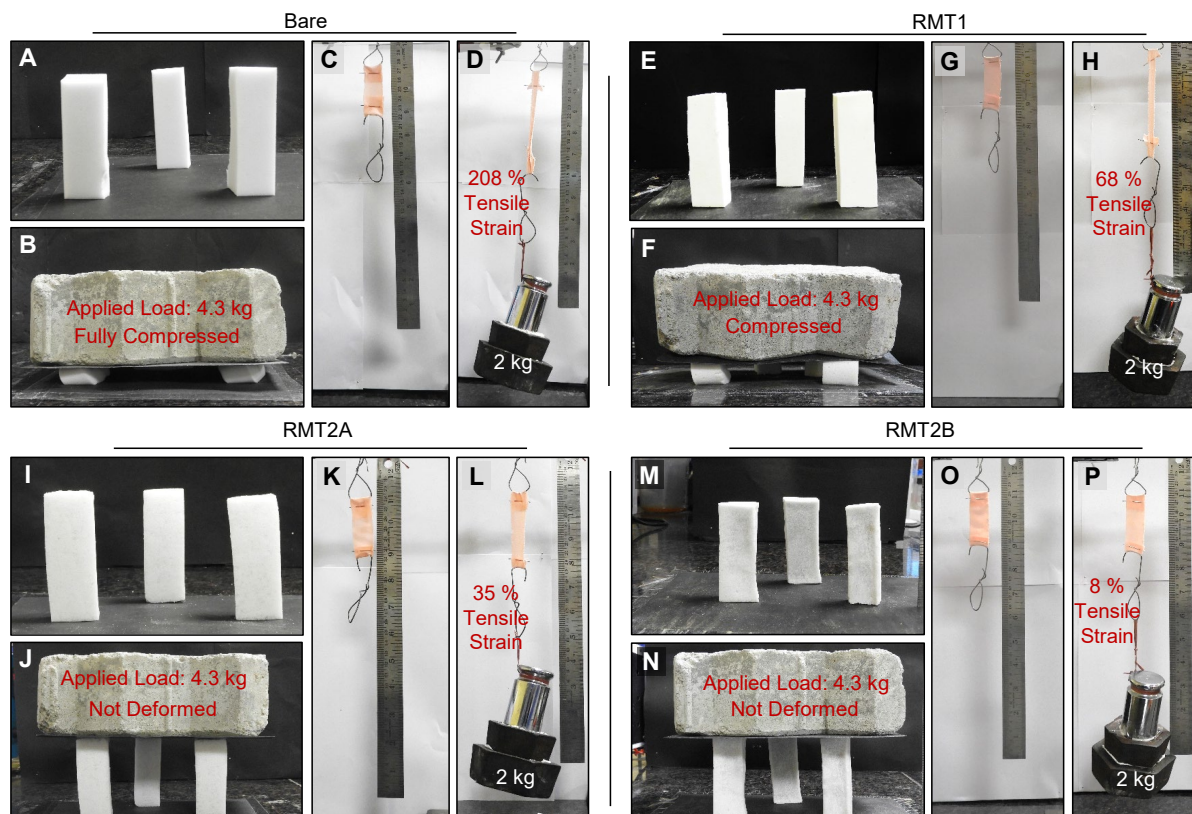


Figure 3.13 A-H) Digital images showing the extent of deformation of Bare and RMT1 coated substrates (melamine formaldehyde sponge and polyurethane fabric) on applying loads. The bare (A, B) and RMT1 coated (E, F) melamine sponge experienced a large amount of compression on applying a load of 4.3 kg, whereas bare (C, D) and RMT1 coated polyurethane fabric (G, H) experienced 208 % and 68 % tensile deformation on applying a load of 2 kg, respectively. I-P) Digital images showing the extent of deformation of RMT2A and RMT2B coated substrates (melamine formaldehyde sponge and polyurethane fabric) on applying loads. The RMT2A (I, J) and RMT2B (M, N) coated melamine foam could withstand the load of 4.3 kg without any deformation, and the polyurethane fabric coated with RMT2A (K, L) and RMT2B (O, P) underwent only 35% and 8% tensile strain upon applying 2 kg load.

respectively, as shown in Figure 3.14A. Moreover, the tensile modulus (1.16 MPa) of the stretchable fibrous substrate followed a very similar trend. The enhancement of the tensile modulus was found to be maximum (215.33 MPa) for the RMT2B coated fibrous substrate— whereas a significantly less (37.27 MPa) increment was noted for the RMT1 coated fibrous substrate, as shown in Figure 3.14B. Eventually, the added cross-linkers in the reaction mixtures (RMT2A/RMT2B) are inherently capable of providing a rigid coating all over the porous and fibrous substrate—and successfully enhanced the compressive and tensile moduli of the selected soft substrates. The covalent crosslinking through the 1, 4-conjugate addition reaction and

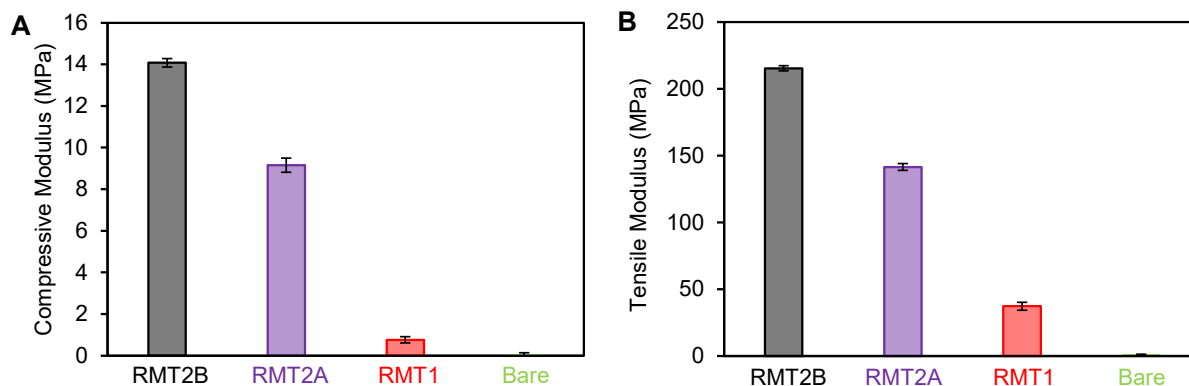


Figure 3.14 A) Bar plot of the compressive modulus values of the melamine sponges coated with the three different reaction mixtures (black (RMT2B), purple (RMT2A), and red (RMT1)) and bare melamine sponge (green). B) Bar plot of the tensile modulus values of the polyurethane fabrics coated with the three different reaction mixtures (black (RMT2B), purple (RMT2A), and red (RMT1)) and bare fabric (green).

selection of appropriate cross-linkers that control local cross-linking density are responsible for tailoring such mechanical properties. In our current study, both the reaction mixtures, i.e. RMT2A and RMT2B, were prepared by maintaining a fixed acrylate to amine ratio (1:1). One molecule of 5-Acl contains five acrylate functional groups, whereas the number of acrylate functional groups in one molecule of 3-Acl is three. Thus, 5-Acl molecules led to more local branching/crosslinking compared to 3-Acl through 1, 4-conjugate addition reaction between the amine and acrylate. Eventually, such covalent cross-linkages caused by 5-Acl enhanced the mechanical properties of the used selected soft substrates. Further, experiments were designed to re-validate the impact of

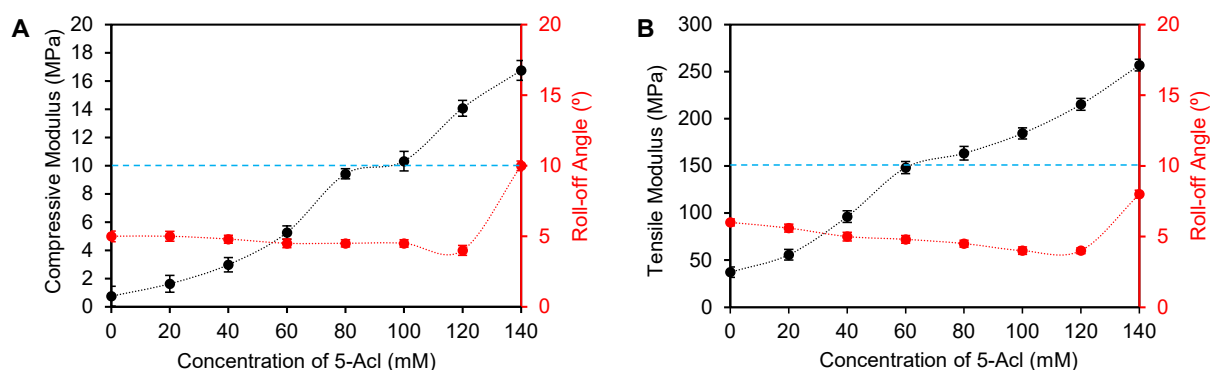


Figure 3.15 A) Plot illustrating the change in compressive modulus and roll-off angle of the melamine sponge coated with RMT2B reaction mixture upon varying the concentration of dipentaerythritol penta-acrylate (5-Acl) from 0 mM to 140 mM. B) Plot illustrating the change in tensile modulus and roll-off angle of the polyurethane fabric coated with the RMT2B reaction mixture upon changing the concentration of dipentaerythritol penta-acrylate (5-Acl) from 0 mM to 140 mM.

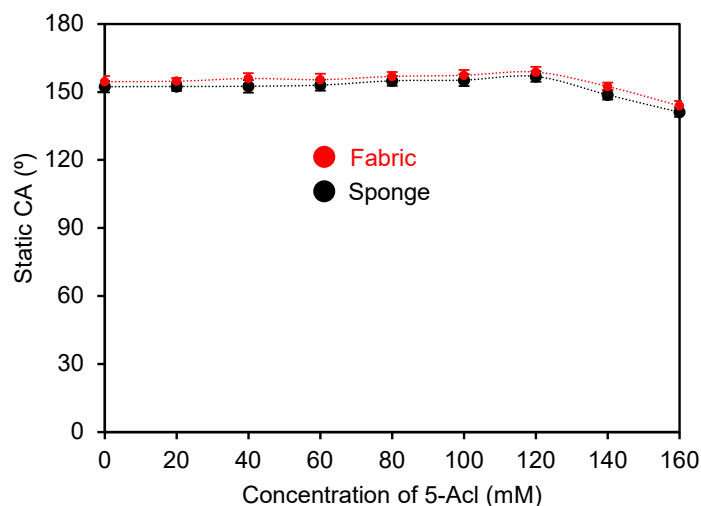


Figure 3.16 Plot showing the change in static contact angle value of beaded water droplet on both coated melamine formaldehyde sponge and polyurethane fabrics on gradually increasing the concentration of 5-Acl from 0 mM to 160 mM in reaction mixture, where the other two reactants were AEAPTMS and ODAc.

the used cross-linkers on tailoring the mechanical properties of the soft and deformable selected substrates. A series of reaction mixtures were prepared by gradually increasing the concentration of 5-Acl from 0 to 160 mM, where the other two reactants were AEAPTMS and ODAc. The individual deposition of these reaction mixtures on the spongy substrate and stretchable fabric yielded superhydrophobic interfaces (static WCAs above 150° and roll-off angles $\leq 10^\circ$)—with gradually increasing compressive modulus (for the selected sponge, Figure 3.15A) and tensile modulus (for the stretchable fabric; Figure 3.15B) on incrementing the content of 5-Acl. It has been observed that the static contact angles and roll-off angles are merely perturbed on changing the concentration of 5-Acl in the reaction mixture from 0 mM to 120 mM. However, a further increment in the concentration (beyond 120 mM) of 5-Acl lowered the static WCA significantly, as shown in Figure 3.16. The reaction mixture with 160 mM 5-Acl failed to provide superhydrophobicity—rather a hydrophobic coating with a static water contact angle of $\sim 140^\circ$ was observed. Such precise control over the mechanical properties through the strategic use of a single small molecule serving as a cross-linker following the facile 1,4-conjugate addition reaction, without perturbing the bio-inspired wettability, is unprecedented—and would be useful for designing various and relevant functional materials. Thus, the current chemical approach provided a single and simple basis for optimizing two distinct and relevant physical properties—(a) mechanical properties and (b) water wettability.

3.3.4 Investigating the Durability of the Coated Substrates and Embedded Water Wettability

Next, the durability of the prepared coatings and their impact on preventing the physical disintegration of the selected soft substrates under severe and identical physical abrasive conditions were studied by adopting some standard and widely accepted abrasions and impact tests. Firstly, the melamine formaldehyde sponges that were individually coated with RMT1, RMT2A and RMT2B were separately exposed to an abrasive sandpaper with an external applied pressure of 25 kPa. The sandpaper moving speed was maintained at 3.5 cm s^{-1} . The impact of the sandpaper abrasion was observed to be distinctly different. Significant physical erosion was noted for the RMT1 coated melamine sponge in comparison to the RMT2B coated melamine sponge under identical abrasive treatment. However, the embedded superhydrophobicity remained unaltered even after the physical disintegration of the coated melamine sponges (Figure 3.17A and B). This simple depiction revealed the existence of bulk superhydrophobicity. On increasing the

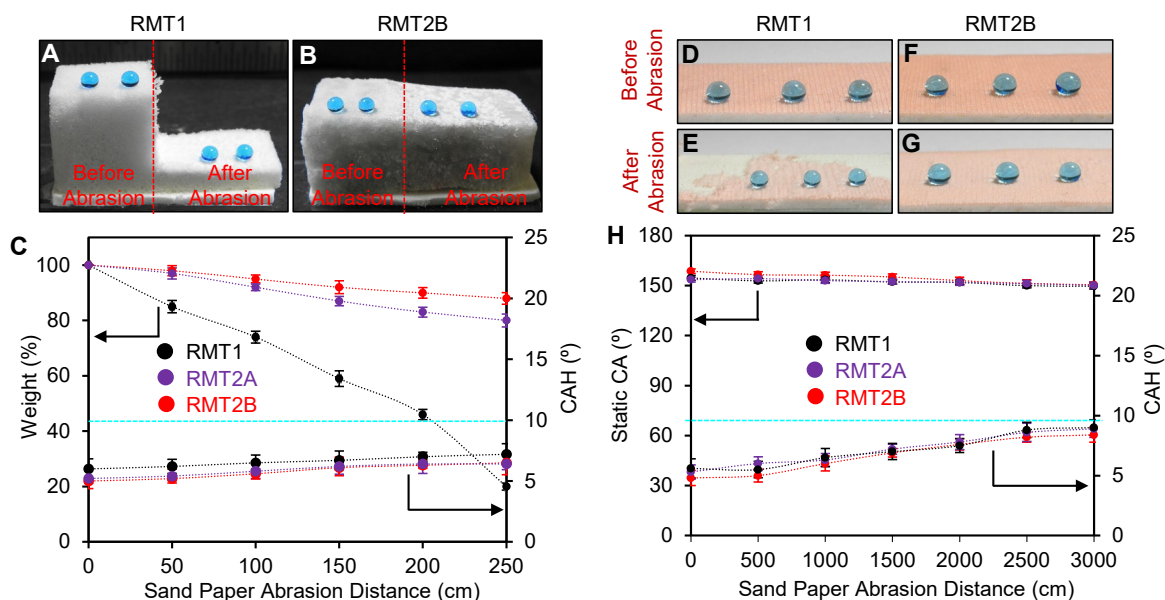


Figure 3.17 A, B) Digital images of melamine formaldehyde sponges coated with RMT1 (A) and RMT2B (B) after sand paper abrasion of 250 cm under an applied pressure of 25 kPa. C) Plot demonstrating the change in weight (%) and contact angle hysteresis (CAH) of the melamine formaldehyde sponges coated with RMT1 (black), RMT2A (purple) and RMT2B (red) upon increasing the sand paper abrasion distance. D-G) Digital images of polyurethane fabrics coated with RMT1 (D, E) and RMT2B (F, G) before (D, F) and after (E, G) sand paper abrasion of 3000 cm. (H) Plot illustrating the change in static contact angle and contact angle hysteresis (CAH) of the polyurethane fabrics coated with RMT1 (black), RMT2A (purple) and RMT2B (red) with sand paper abrasion distance.

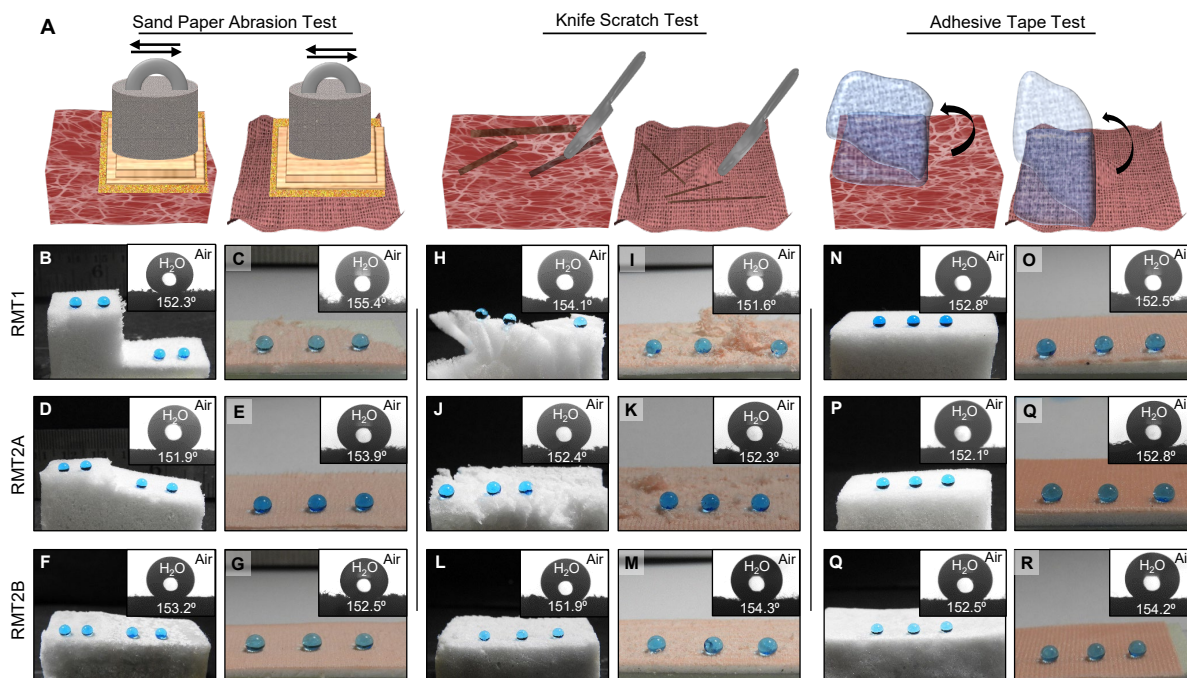


Figure 3.18 Comparing the durability of superhydrophobic materials that were derived from RMT1, RMT2A and RMT2B. A) Schematic representation of different physical abrasive exposures- Sand paper abrasion, Knife scratch test and adhesive tape test performed on the coated substrates. B-G) Digital images and contact angle images (inset) of substrates (melamine sponge and polyurethane fabric) coated with three different reaction mixtures RMT1 (B, C), RMT2A (D, E) and RMT2B (F, G) after sand paper abrasion. H-M) Digital images and contact angle images (inset) of substrates (melamine sponge and polyurethane fabric) coated with three different reaction mixtures RMT1 (H, I), RMT2A (J, K) and RMT2B (L, M) after knife scratch test for multiple times. N-R) Digital images and contact angle images (inset) of substrates (melamine sponge and polyurethane fabric) coated with three different reaction mixtures RMT1 (N, O), RMT2A (P, Q) and RMT2B (Q, R) after adhesive tape test for 250 times.

abrasion distance, the percentages (%) of weight loss of the two distinctly coated sponges were noticed to be significantly different as shown in Figure 3.17C. A drastic (80%) weight loss was observed for the RMT1 coated sponge, whereas only 12% weight loss was estimated for the RMT2B coated sponge after incurring a sandpaper abrasion distance of 250 cm under the applied external pressure of 25 kPa as depicted in Figure 3.17C. Under identical abrasive conditions, the physical erosion of the RMT2A coated sponge was found to be slightly more (~20% weight loss) in comparison to the RMT2B coated sponge (12% weight loss). However, the damaged interface continued to display extreme water repellence with WCAs above 150° and CAH below 10° (see Figure 3.17C). On the other hand, stretchable fibrous substrates that were independently coated with RMT1, RMT2A and RMT2B were exposed to the same sandpaper abrasion. After exposing

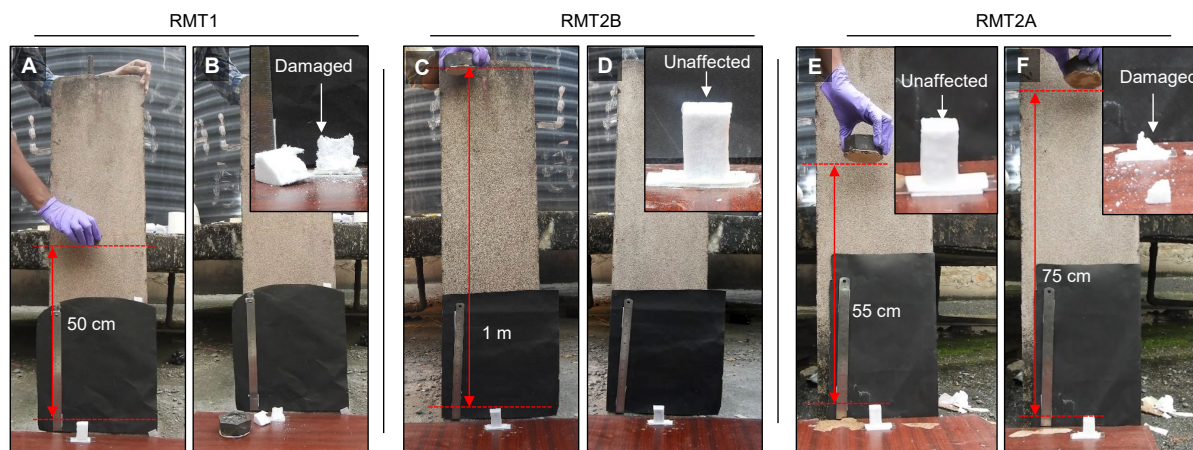


Figure 3.19 Digital images showing the impact of 1 kg weight on melamine foams coated with three different reaction mixtures RMT1 (A, B), RMT2B (C, D) and RMT2A (E, F) from different heights (50 cm for the RMT1 coated melamine foam (A, B), 1 m for the RMT2B coated melamine foam (C, D), 55 cm and 75 cm for the RMT2A coated melamine foam (E, F).

the coated fibrous substrates to identical sandpaper abrasion distance (3000 cm), the RMT1 coated substrate was significantly damaged, and different parts of the coated substrate were torn apart while both RMT2A and RMT2B coated substrates remained intact. Even after 3000 cm of sandpaper abrasion under the applied external pressure of 25 kPa, both RMT1 and RMT2B coated substrates continued to display non-adhesive super water repellency with static WCA above 150° and contact angle hysteresis below 10° as shown in Figure 3.17D-H. Thereafter, the coated interfaces that were individually derived from RMT2A and RMT2B were exposed to various other abrasion tests—including the knife scratch test and adhesive tape peeling test with 500 g of external load multiple times—and the fate of these distinctly coated substrates were very similar

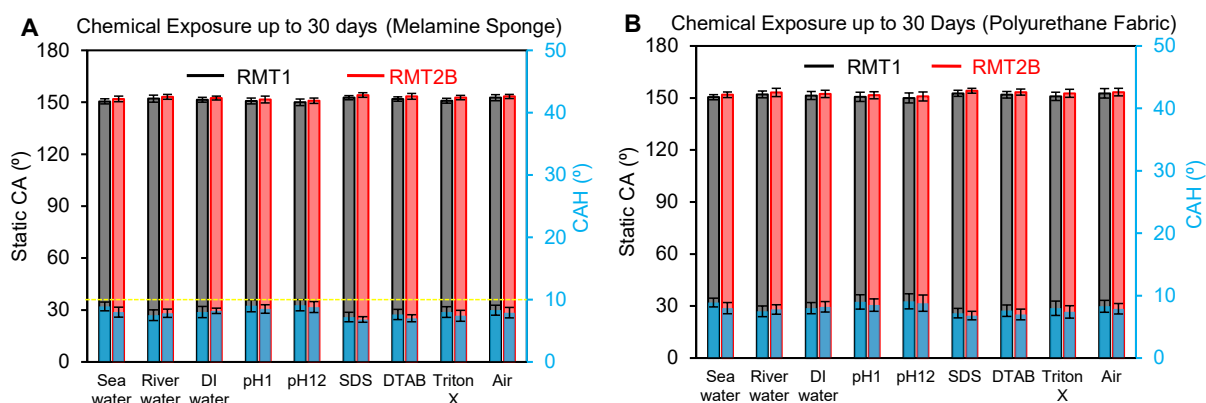


Figure 3.20 Bar plot illustrating the effect of continuous exposure of 30 days to various chemicals on melamine sponge (A) and polyurethane fabric (B) coated with RMT1 (black) and RMT2B (red).

as shown in Figure 3.18A-R. Further, the RMT1, RMT2A and RMT2B coated melamine formaldehyde sponges were exposed to the impact of external loads from different distances. While the RMT1 coated sponge was broken into pieces after dropping the 1 kg load from a 50 cm distance, the RMT2B (having 5-Acl as the cross-linker) coated sponge was efficient in tolerating the impact of dropping the same 1 kg load from a distance of 1 m—without causing any noticeable physical damage to the material as shown in Figure 3.19A-D. In comparison, the 3-Acl-assisted reaction mixture (RMT2A) failed to survive an impact of 1 kg load from a distance of 75 cm distance (Figure 3.19E, F). This simple demonstration confirmed that the current coating approach could (1) modulate the mechanical properties and (2) prevent the physical disintegration of the spongy and soft substrates under severe and challenging circumstances. Furthermore, both the RMT1 and RMT2B coated fabrics and sponges were exposed to various and complex aqueous phases—including sea water, river water, alkaline water (pH 12), acidic water (pH 1), and water contaminated with surfactants (SDS, DTAB, Triton X) for 30 days. However, the coated interfaces were efficient in successfully tolerating the exposure to these different and complex chemical conditions and displayed extreme water repellency with static WCAs above 150° and contact angle hysteresis below 10° as shown in Figure 3.20A and B. The embedded superhydrophobicity of the prepared materials remained intact after continuous UV illumination (at $\lambda_{\max}$ – 254 nm, 8 W and 365 nm, 8 W) for 7 days as shown in Figure 3.21A. The superhydrophobic fabrics that were derived

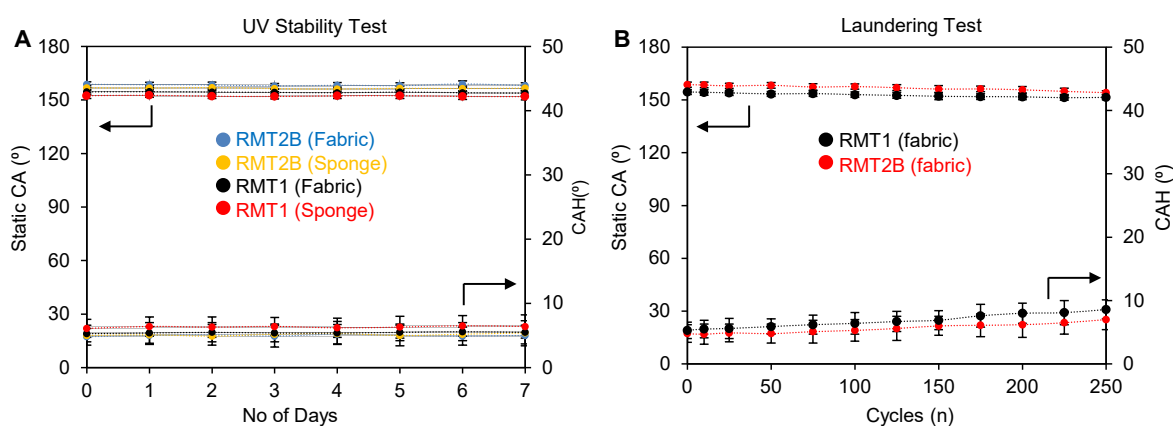


Figure 3.21 A) Plot showing the change in static contact angles (CA) and contact angle hysteresis (CAH) of beaded water droplets on RMT2B coated fabric (red) and sponge (black), RMT2A coated fabric (blue) and sponge (brown), RMT1 coated fabric (green) and sponge (purple) after exposure to UV radiation ($\lambda_{\max}$ – 254 nm and 365 nm) for continuous 7 days. B) Plot accounting for the change in static contact angles (CA) and contact angle hysteresis (CAH) of beaded water droplets on RMT1 (black) and RMT2B (red) coated fabric during repetitive washing test (250 cycles).

from RMT1 and RMT2B survived the standard washing test (AATCC Test Method 61-2006 Test No 2A) for 250 cycles. The embedded superhydrophobic coatings continued to repel the beaded water droplet with static contact angles above 150° and contact angle hysteresis below 10° as shown in Figure 3.21B. Thus, both deformable and non-deformable coatings that were derived from RMT1 and RMT2B displayed highly tolerant superhydrophobicity under different chemically complex conditions. The synthesized tolerant and hard superhydrophobic coating that provided resistance to physical abrasion under challenging conditions would be interesting for various other outdoor applications—including energy harvesting, desalination, droplet condensation, developing smart textiles and concrete etc.^{32–34}

3.4. Conclusions

In conclusion, the 1,4-conjugate addition reaction between amine and acrylate groups has been extended to achieve both tolerant superhydrophobicity and customized mechanical properties in a single step through strategic and controlled association of an appropriate cross-linker (i.e., 5-Acl/3-Acl) in the selected reaction mixture of small molecules (i.e., AEAPTMS and ODAc). The selected AEAPTMS acted as a binder to the selected substrates, and ODAc allowed associating the essentially low surface energy that confers superhydrophobicity. Further, the strategic use of 5-Acl/3-Acl modulated the compressive/tensile modulus of the selected soft and deformable substrates. Thus, a simple chemical reaction between the strategically selected reactants allowed for achieving ‘tolerant and hard’ superhydrophobic coatings on soft and deformable substrates to prevent their physical erosion and rupture in practically relevant and severe outdoor settings.

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Chapter 4: Design of a Self-Cleanable Multilevel Anticounterfeiting Interface through Covalent Chemical Modulation

Counterfeit products have posed a significant threat to consumers' safety and the global economy. To address this issue, extensive studies have been exploring the use of coatings with unclonable, microscale features for authentication purposes. However, the ease of readout, and the stability of these features against water, deposited dust, and wear, which are required for practical use, remain challenging. Here I report a novel class of chemically functionalizable coatings with a combination of a physically unclonable porous topography and distinct physiochemical properties (e.g., fluorescence, water wettability, and water adhesion) obtained through orthogonal chemical modifications (i.e., 1,4-conjugate addition reaction and Schiff-base reaction at ambient conditions). Unprecedentedly, a self-cleanable and physically unclonable coating is introduced to develop a multilevel anticounterfeiting interface. I demonstrate that the authentication of the fluorescent porous topography can be verified using deep learning. More importantly, the spatially selective chemical modifications can be read with the naked eye via underwater exposure and UV light illumination. Overall, the results reported in this work provide a facile basis for designing functional surfaces capable of independent and multilevel decryption of authenticity.

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4.1 Introduction

The counterfeiting of intellectual property and commercial goods is a well-recognized threat to society, the economy, and consumers' health across the world.^{1–5} The joint report by the Organisation for Economic Co-operation and Development (OECD) and the European Union Intellectual Property Office (EUIPO) reveals that counterfeit goods cost the global economy around 461 billion dollars annually.² Previous approaches used substrate structures,^{6–8} surface tags,^{9,10} embedded tags,^{11,12} and patterned interfaces^{13,14} to combat the growing challenges associated with counterfeiting. Many of these approaches failed to provide adequate security because they were easily cloneable and thus did not provide the needed protection against counterfeiting.¹⁵ As a result, there has been an emergent interest in developing physically unclonable interfaces for use in anticounterfeiting.^{16–28} For example, functional nanoparticles,^{16–18} Raman active materials,²⁰ the crumpling of nanomaterials,¹⁹ the wrinkling of polymers,^{21,22} composite lattice photonic crystals,²³ inorganic and organic luminescent materials,^{24–27} and fluorescent protein microparticles²⁸ have been utilized to attain physically unclonable interfaces. While the recent development of machine learning techniques provides a reliable means to verify the authenticity of the above physically unclonable interfaces, it usually requires sophisticated instrumentation to obtain relevant information about the microscale unclonable features (e.g., optical/electronic microscopy imaging, Raman imaging, and electrical measurement). Hence, designing and developing unclonable materials that allow an instrument-free and easy-to-read technique is essential for reliable and convenient anticounterfeit applications.

In this context, a patterned interface with a combination of distinct physical properties would provide a basis for developing a multilevel anticounterfeit technique that enables orthogonal and instrument-free information decryption and readout, while still allowing microscopy imaging-based machine learning. For example, interfaces with microscale topographies, such as those found on the lotus leaf and rose petal, have been demonstrated to enable extreme water repellence.^{29–33} Based on the Cassie–Baxter model,³⁴ the extreme water repellence of these bio-inspired interfaces can be attributed to the presence of external third phase, i.e. air phase trapped between the solid and water phase. However, the same topography with a high surface energy is superhydrophilic. Previously, two extremes of such water wettability, i.e., superhydrophobicity and superhydrophilicity, have been utilized for demonstrating anticounterfeiting applications, where the selective infiltration of the aqueous phase on the hydrophilic area allows for identification of

the pattern with the naked eye.^{35,36} However, one of the major limitations of this approach is that the selective infiltration of water wets the pattern—and it remains visible even after being removed from the aqueous phase. Moreover, such wet interfaces can be easily contaminated by dust and dirt. Recent studies have shown that modifying either the topography or chemistry of superhydrophobic interfaces can give rise to both adhesive and non-adhesive superhydrophobicity (characterized by contact angle hysteresis greater or less than 10° , respectively, and a contact angle greater than 150°) with varying amounts of trapped air, modulating the mobility of water droplets

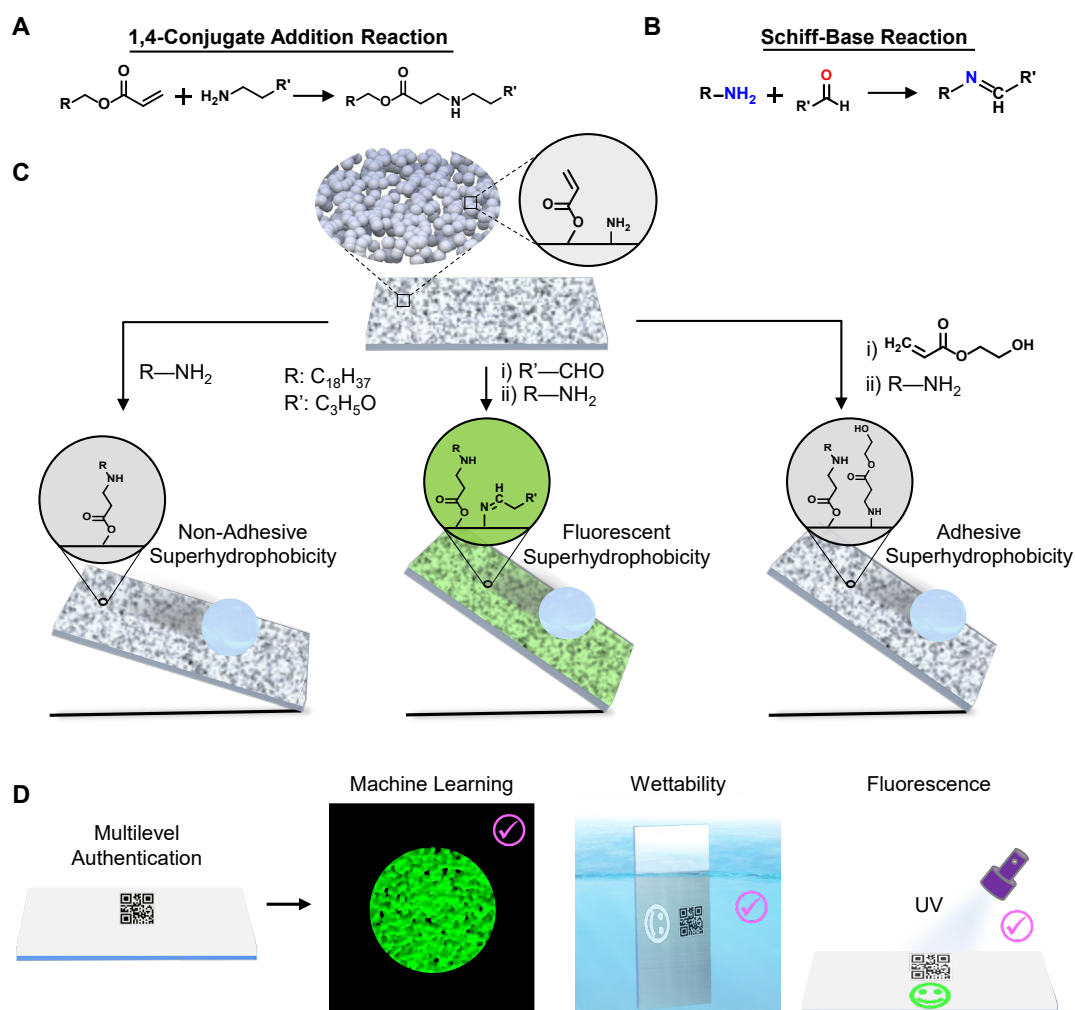


Figure 4.1 Design of multilevel anticounterfeiting interface based on chemically functionalizable porous polymeric coating. A, B) 1,4-conjugate addition reaction (A) between a primary amine and acrylate functional groups and the Schiff base reaction (B) between an aldehyde and primary amine functional groups. C) Scheme of different post-chemical modifications for non-adhesive, adhesive, and fluorescent superhydrophobicity. D) Schematic depiction of three distinct authentication steps to identify the legitimacy of a quick response (QR) code on the porous polymeric coating.

on these surfaces.^{37–43} However, such adhesive and non-adhesive superhydrophobic interfaces have not been explored in the context of anticounterfeiting. Therefore, I hypothesize that by exploiting the above phenomena, I can design and synthesize self-cleaning coatings with adhesive and non-adhesive superhydrophobic patterns that are invisible in the air but are visible underwater to the naked eye, allowing for instrument-free information decryption. Furthermore, the strategic combination of adhesive and non-adhesive water wettability, optical properties, and unclonable microscale topography would enable the development of a new class of physically unclonable surfaces for multilevel information encryption and decryption.

In this work, I report a method to synthesize and modify a dual chemically functionalizable porous polymeric coating using a 1, 4-conjugated addition and Schiff-base reaction, as shown in Figure 4.1. The inherent porous topography of the prepared polymeric coating gives rise to unclonable features that can be decrypted using microscopy imaging-based machine learning. On the other hand, the reactive moieties in the coating, i.e., amine and acrylate, play an important role in determining the amount of air trapped in the coating, which confers both water-repellence and the condition-dependent appearance of patterns, such as being invisible in the air, but visible underwater. Moreover, the spatially selective post-modulation of the above coating through the formation of imine bonds embeds fluorescence that can be read out upon UV illumination. Overall, this novel class of anticounterfeiting interfaces can be decoded through multilevel authentication routes: besides the machine learning-based decryption of the random surface topography, the readout can occur through visual inspection during the exposure of the patterned interface to an aqueous phase or UV light.

4.2. Experimental Section

4.2.1. Materials Required

Branched poly(ethyleneimine) (BPEI; molecular weight ~ 25,000 Da), 2-hydroxy acrylate (HA), and octadecyl amine (ODA) were purchased from Sigma-Aldrich, India. Glutaraldehyde (Glu; 25 % aqueous solution) was purchased from Merck, India. Glucamine was purchased from TCI, India. 1-Heptanol was purchased from Alfa-Aesar, India. Tetrahydrofuran (THF) was purchased from RANKEM, India. Microscope glass slides were obtained from Jain Scientific Glass Works, India. Details of other chemicals are provided in Chapter 2.

4.2.2 Characterization

A dynamic light scattering (DLS) study was conducted using a Zetasizer Nano ZS90 instrument (ZEN3690). Phase contrast and fluorescence microscopy images were recorded using a ZEISS Axio Vert.A1 inverted microscope. Solid state fluorescence spectra were recorded in Perkin-Elmer Lamda 750 spectrophotometer. Details of other characterization techniques used in this work are given in Chapter 2.

4.2.3 Preparation of Functionalizable Porous Coating

The reactive porous polymeric coating was prepared via the spray deposition of reactive nano complex dispersions on various substrates, i.e., microscopic glass slide, aluminum foil, plastic, paper, and wood. The first step involved the preparation of the reactive nano complex solution in heptanol by mixing 10 mL of 5-Acl (1.3 g/10 mL) and 3 mL of BPEI (0.5 g/10 mL) in a spraying bottle and shaking vigorously for 5 min until the solution becomes turbid, indicating the formation of the nanocomplex. Next, the nano-complex dispersion (13 mL) was uniformly spray deposited onto the selected substrates over an area of 130 cm² from a distance of 10 cm. After the deposition, the coated substrates were dried in air overnight, followed by washing with methanol.

4.2.4 Post-Functionalization of Reactive Coating with Small Molecules

The reactive porous polymeric coatings were modified further by post-functionalization with various small molecules containing different functional groups, i.e., aldehyde, primary amine, and acrylate functional groups. In the post-functionalization treatment, the coatings were individually placed in the solution containing the desired small molecules for 12 h (5 mg/mL of ODA in THF; 80 mg/mL of HA and Glu in water). Afterwards, the coatings were thoroughly washed with ethanol and dried in air.

4.2.5 Fabrication of Different Patterned Interfaces

The prepared hydrophobic reactive porous coating was first exposed to an HA aqueous solution for hydrophilic patterning on the coating. After drying, the patterned coating was washed repeatedly with ethanol to remove excess reactants. Then, the coating was placed in a THF solution containing ODA overnight, followed by rinsing thoroughly with THF to remove excess ODA. This successive modification of the prepared coating with HA and ODA generates a patterned interface comprising adhesive and nonadhesive superhydrophobicity, respectively. The same procedure was followed to prepare a UV active patterned interface that also displays a pattern of adhesive-nonadhesive superhydrophobicity following the spatially selective modification of the reactive

porous coating with Glu instead of HA before treatment with ODA.

Moreover, before post-modification with ODA, the spatially selective modification of the same reactive coating with glucamine instead of HA yielded patterned interfaces with two extremes of wettability (superhydrophilicity and superhydrophobicity). The spatially selective glucamine modification provided a hydrophilic region, and the ODA treatment provided the superhydrophobic regions.

For the QR code-printed patterned interfaces, aluminum foil was used as the substrate. The same procedure discussed above was followed to obtain patterned interfaces coated on aluminum foil. Next, the QR code showing “IITG” was printed on the aluminum foil-supported patterned interface using a laser printer.

4.2.6 Particle Size Analysis

The growth and size distributions of the nano complexes of the reaction mixture of 5-Acl and BPEI in heptanol and ethanol were characterized with DLS. In order to determine the size of the nanocomplexes formed as the reaction progressed, the reaction mixture of 5-Acl and BPEI at different times was diluted 200 times in ethanol. For every solution, at least 6 measurements were recorded.

4.2.7 Self-Cleaning Performance

The self-cleaning performance was evaluated using a coating containing deposited dust particles placed under a stream of water. Rolling water droplets over the coating resulted in the collection of the deposited dust particles, showing that the spatially and selectively modified, with either HA@ODA or Glu@ODA, surfaces could be easily cleaned. However, other modifications failed to display the self-cleaning ability.

4.2.8 Convolution Neural Network Architecture

In this study, I utilized a convolution neural network (CNN) model to automate the authentication of the porous coating fluorescent spots. The CNN model architecture comprised four 2-dimensional convolution layers (Conv2D) with 128, 256, 256, and 512 neurons, respectively; each Conv2D was followed by a rectified linear unit (ReLU) activation function for the elementwise mapping of the input to yield an activated object.⁴⁹ Also, a max pooling layer was added after each ReLU activation function for dimension reduction to make the learned object invariant to small-length scale perturbations.⁵⁰ A fully dense layer containing 512 neurons was added to the four-layer convolution block, followed by a 50% dropout layer as a regularization mechanism to control

overfitting.⁵¹ Afterward, the output from the dropout layer was passed to a dense layer containing 1 neuron with a SoftMax activation function for predicting the probabilities for the binary (Real and Fake) image classification.

4.2.9 Training and Serving the CNN Model

Micrographs of the porous coating fluorescence spots were converted to grayscale and fed into the CNN model described above. For training the CNN model, I used a validation to training data ratio of 0.2, a 5 categorical cross-entropy loss function, and an Adam optimizer. The training and validation accuracy and loss results are shown in Figure 4.6. Afterwards, the model was saved, containerized using docker, and deployed on a server to allow for the automated validation of the porous fluorescence coating authenticity.

4.2.10 Tissue Paper Abrasion

In the tissue paper abrasion test, the superhydrophobic interface with fluorescent dots was rubbed manually with tissue paper in a back-and-forth motion with 100 g of load on top of it for several cycles. Thereafter, fluorescence microscope imaging was performed, and microscopic images of fluorescent dots acquired from this abraded surface were used further for machine learning study.

4.3 Results and Discussion

4.3.1 Machine Learning Authentication of the Fluorescent Superhydrophobic Pattern

I prepared a highly porous and chemically functionalizable coating through a 1, 4-conjugate addition reaction^{41, 44} between branched polyethyleneimine (BPEI; molecular weight ~25,000 Da) and dipentaerythritol penta-acrylate (5-Acl) in heptanol. The BPEI and 5-Acl mixture in heptanol was sprayed on a substrate to obtain a chemically functionalizable and highly porous polymeric coating. The field emission scanning electron microscope (FESEM) images in Figure 4.2A and B confirm the existence of a highly porous topography in which granular domains aggregate randomly during the sol–gel conversion of BPEI and 5-Acl. The existence of residual acrylate groups in the coating was verified by two characteristic IR peaks for the ester carbonyl stretching and the symmetric deformation of the vinylic C–H bond at 1730 cm^{-1} and 1410 cm^{-1} , respectively, in Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra (Figure 4.2C). As shown in Figure 4.1, the highly porous network of aggregated granular domains was further chemically modulated to confer fluorescence and bio-inspired superhydrophobicity. In the past, glutaraldehyde crosslinking has been used to achieve auto-fluorescence in biomedical applications.⁴⁵ Inspired by this earlier report, the prepared polymeric coating was covalently

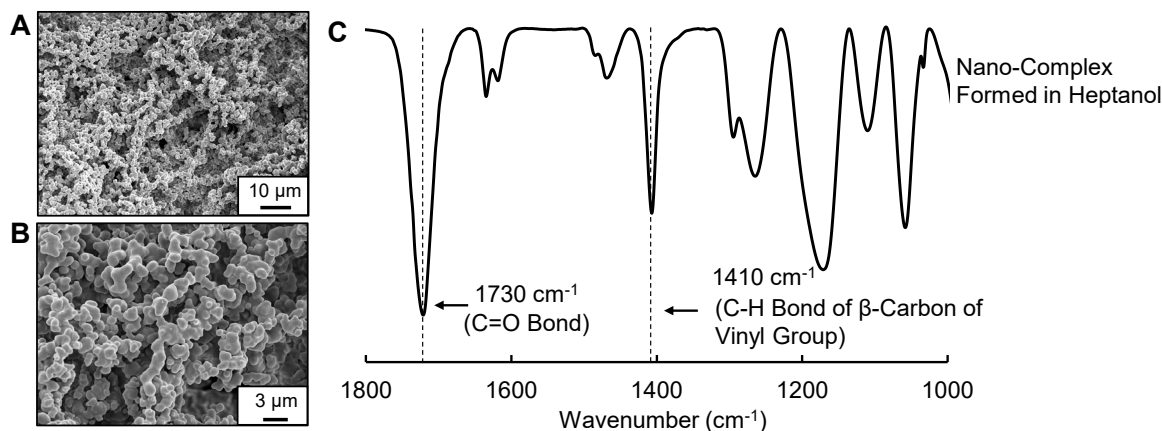


Figure 4.2 A, B) Field emission scanning electron microscopy (FESEM) images of the porous polymeric coatings (A and B). C) ATR-FTIR spectra of the BPEI/5-Acl nanocomplexes prepared in heptanol. Characteristic IR peaks at 1730 cm^{-1} and 1410 cm^{-1} corresponding to the carbonyl stretching of ester groups and the symmetric deformation of the vinylic C–H bonds, respectively, indicating the presence of residual acrylate groups in the reactive nano-complexes.

modified with glutaraldehyde (Glu) through imine bond formation to introduce fluorescence (due to the $n\text{-p}^*$ transitions of the imine bond).⁴⁶ Figure 4.3A and B show an intense fluorescence signal after modifying the polymeric coating with Glu. The solid-state fluorescence spectrum of glutamodified coating showed an emission peak at 462 nm when excited at 369 nm , as shown in Figure 4.3C. An additional IR signature was noted at 1680 cm^{-1} after the post-modification of the porous polymeric coating with Glu, signifying the formation of imine bonds through the Schiff-base reaction between the residual amine group of the polymeric coating and the aldehyde group of glutaraldehyde, as shown in Figure 4.3D and 4.1B. In contrast, the modification of the same reactive coating with hexyl acrylate (HLA) prior to Glu treatment exhibited no fluorescence signal (Figure 4.4B). Even consecutive treatment with HLA and Glu did not lead to formation of fluorescent imine bond at 1680 cm^{-1} , as evidenced in Fig. 4.3D. The association of fluorescence with the randomly porous topography provides physically unclonable features that can be visualized under a fluorescence microscope. Specifically, I spatially patterned the coating through chemical modification with an aqueous droplet of Glu (concentration of 80 mg mL^{-1}). The inherent hydrophobicity of the prepared polymeric coating (water contact angle of $\sim 128^\circ$; Figure 4.5A) restricted the arbitrary spreading of the tiny beaded aqueous droplets on the highly porous coating during the spatially selective chemical modification process. Eventually, the Glu-modified pattern appeared only under UV light (365 nm) exposure but not under visible light, as evidenced by the

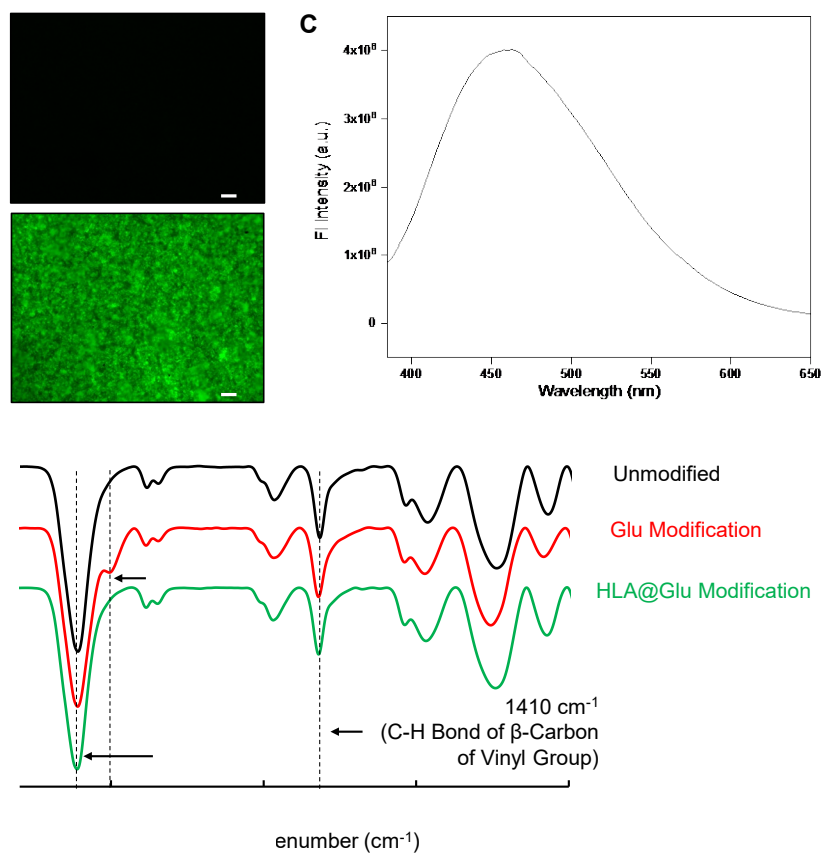


Figure 4.3 A, B) Fluorescence micrographs of unmodified (A) and glutaraldehyde-modified (Glu) porous polymeric coatings (B). C) Solid state fluorescence spectrum of glutaraldehyde-modified (Glu) porous polymeric. D) Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra of the porous polymeric coatings before modification (black), after chemical modification with glutaraldehyde (Glu; red), and after consecutive modification with hexyl acrylate (HLA) followed by Glu treatment (HLA@Glu; green). The successful Glu chemical modification was confirmed by the appearance of a 1680 cm⁻¹ peak corresponding to imine (C=N) bond stretching.

word ‘REAL’ in Figure 4.5B-D. Next, I demonstrated that the unique topography of each porous coating could be used to automate its authentication, making it suitable for machine learning-aided anticounterfeiting. Specifically, I automated the process for authenticating the fluorescent spots on the porous polymer coatings by training a convolution neural network (CNN)^{47,49–51} with images of the fluorescence spots obtained using a fluorescence microscope, as shown in Figure 4.6A. Specifically, some porous coating fluorescence spots were added to a database classified as ‘real’, including Images a1–a5 in Figure 4.6B. After training the CNN model with images in the ‘real’ database, the robustness of the model prediction was evaluated using Image a1 with different exposures (Images b1–b5) and Image a3 after several cycles of tissue paper abrasion (Images c1–

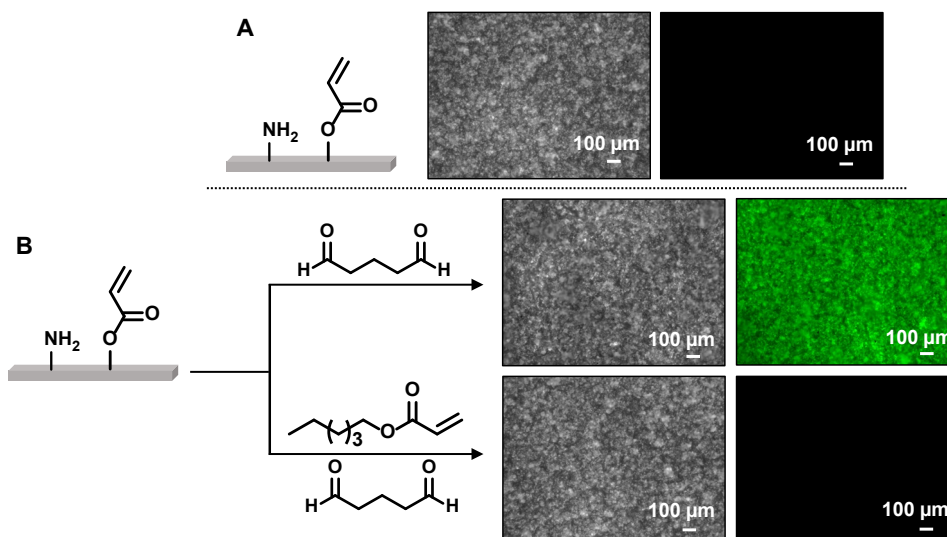


Figure 4.4 A, B) Phase contrast and fluorescence micrographs of functionalizable and porous polymeric coating before (A) and after (B) mono (glucamine (Glu)) and dual (hexylacrylate (HLA)) followed by Glu post-modification. The inherently non-fluorescent reactive porous coating (A) shows green fluorescence only after successful post-modification with Glu (B). However, the coating does not fluoresce after successive modifications with HLA and Glu, as the available residual amine group is consumed during HLA modification and prevents post-covalent modification with Glu.

c5). The model recognized all these images as real with a probability of ~ 1 , as shown in Figure 4.6C and E. In addition, the model identified images that were not in the database, evidenced by the negligible predicted probability, which is termed as “probability of being real” (Figure 4.6D). These results demonstrate that the porous coating’s unique and unclonable topography enables its use for machine learning-enabled anticounterfeiting.

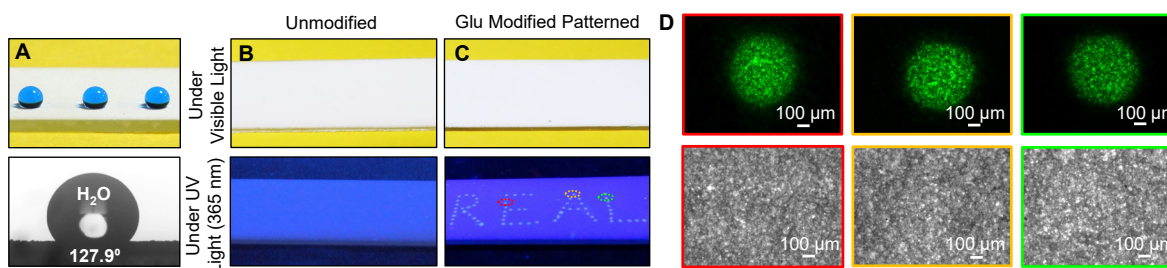


Figure 4.5 A) Photograph of beaded water droplets (dyed with methylene blue) and the static contact angle measurement on an unmodified porous polymeric coating. The volume of the beaded water droplets was 12 μL for the photograph and 5 μL for the contact angle goniometer image. B, C) Photographs of unmodified (B) and ‘REAL’ patterned coating (C) through selective modification with glutaraldehyde under visible light and UV illumination (365 nm). (D) Fluorescence and phase contrast micrographs of three different regions of the ‘REAL’ pattern in (C).

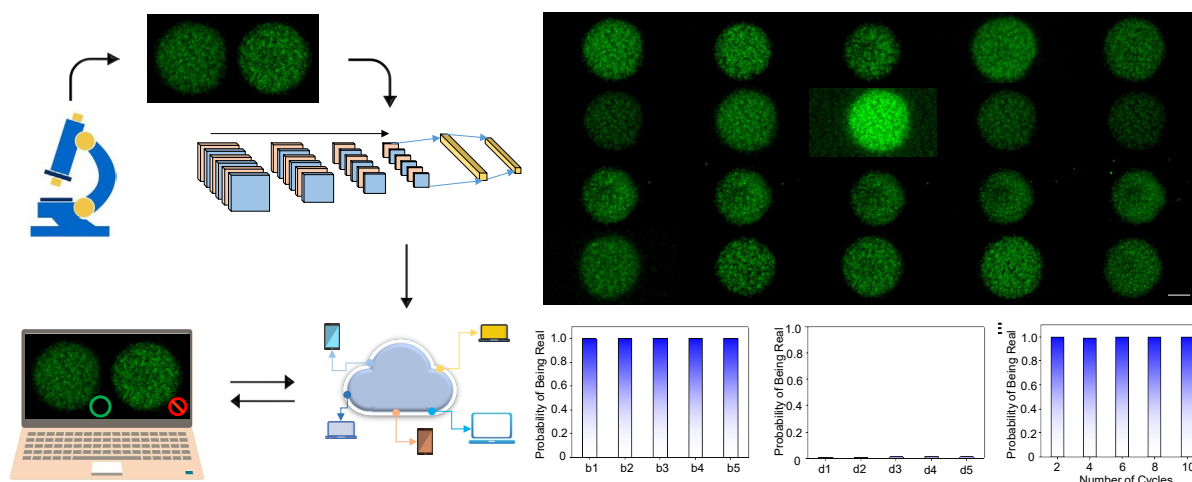


Figure 4.6 Authentication of fluorescent porous polymeric coatings through machine learning. A) Schematic demonstrating the process for the automatic authentication of the fluorescence spots on the porous polymeric coatings. B) Fluorescence micrographs of the fluorescence spots: Images a1–a5 in the ‘real’ database, Images b1–b5 represent a1 images with different exposure levels, Images c1–c5 represent a3 images that have undergone varying cycles of abrasion, and Images d1–d5 represent images that are not in the ‘real’ database. C–E) Probability of the CNN model prediction of Images b1–b5 (C), d1–d5 (D), and c1–c5 (E) belonging to the ‘real’ database.

4.3.2. Preparation of Adhesive/Non-Adhesive Superhydrophobic Pattern

While the above results demonstrate authenticity verification through machine learning, this approach requires sophisticated instrumentation and specialized expertise. I hypothesized that the residual reactivity of the porous polymer coating (e.g., primary amine and acrylate groups) provides an opportunity for the decryption of the hidden information with the naked eye. The polymeric coating was selectively modified through a 1, 4-conjugate addition reaction to achieve a superhydrophobic interface that displayed patterns with distinct amounts of trapped air. The modification with octadecyl amine (ODA) resulted in a non-adhesive superhydrophobicity with a water contact angle of $\sim 158^\circ$ and a roll-off angle of $\sim 7^\circ$ (Figure 4.8A and 4.9A). Alternatively, successive post-modification of the coating with 2-hydroxy acrylate (HA) and ODA (denoted as HA@ODA) resulted in an adhesive superhydrophobicity with a water contact angle of $\sim 151^\circ$ and a roll-off angle of $\sim 15^\circ$, as shown in Figure 4.8B–D and 4.9B. The reaction of HA and ODA with the residual amine and acrylate groups of the coating, respectively, through a 1, 4-conjugate addition reaction was verified by FTIR-ATR, as shown in Figure 4.8E. Next, I measured the adhesive force of beaded water droplets on the ODA and HA@ODA modified superhydrophobic coatings. As shown in Figure 4.9C, the adhesive force on the HA@ODA-modified coating (104

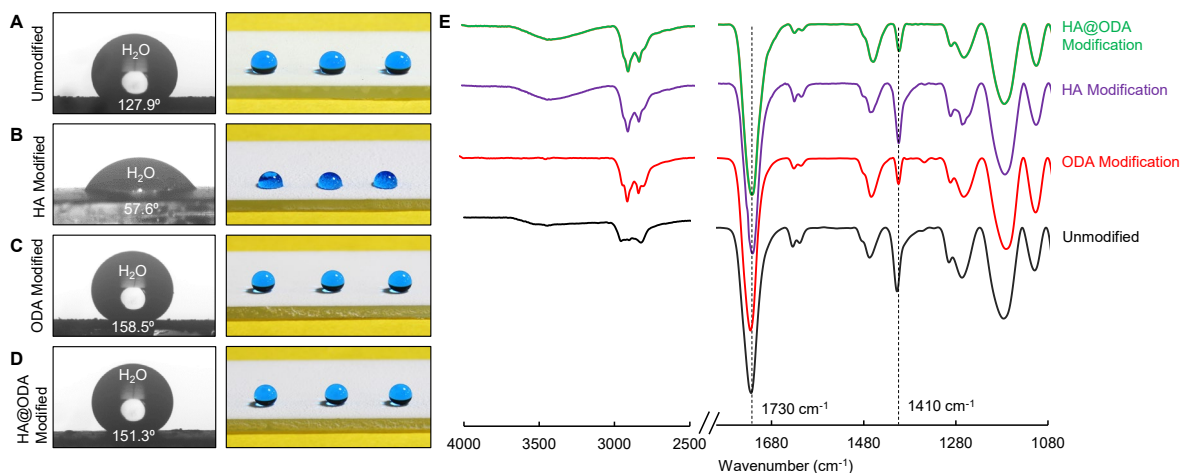


Figure 4.7 Static contact angle images and photographs of a beaded water droplet on unmodified (A), 2-hydroxy acrylate (HA) (B), octadecyl amine (ODA) (C), and HA@ODA (D) modified porous polymeric coatings. The volume of the beaded water droplets was 12 μL for the photograph and 5 μL for the contact angle goniometer image. E) FTIR-ATR spectra of unmodified (black), HA (purple) modified, ODA (red) modified, and HA@ODA (green) modified porous polymeric coatings. The FTIR-ATR spectra reveal changes in the intensity of certain infrared (IR) peaks after the modification process. After modifying with ODA, the intensity of the IR peak at 1410 cm^{-1} , associated with vinylic C–H bonds, decreased significantly. However, modifying with HA resulted in the appearance of an IR peak at 3400 cm^{-1} , associated with O–H stretching arising from the association of the HA hydroxyl group to the postmodified coating. In contrast, the characteristic IR signature for the symmetric deformation of the vinylic C–H bond at 1410 cm^{-1} remained unchanged. Dual modification with both HA and ODA caused the appearance of the IR peak at 3400 cm^{-1} and the decrease in the intensity of the IR peak at 1410 cm^{-1} . These changes indicated that the modification process was successful and altered the properties of the porous polymeric coating.

μN) was almost two times than that of the ODA-modified coating (57 μN). Based on the Cassie–Baxter theory, this change in water adhesion is caused by the alteration of the fraction of contact area between the beaded water and trapped air,³⁴ which is estimated as:

$$\cos \theta_{CB} = f_s \cos \theta - f_a \quad (4.1)$$

where θ_{CB} and θ are the static contact angle of a beaded water droplet on a porous coating and a smooth coating, respectively, and f_s denotes the fraction of contact area between the coating and water droplet. The fraction of contact area between the metastable trapped air and water droplet is referred to as f_a , where $f_s + f_a = 1$. In comparison to ODA modified coating, f_a was calculated to be 5.3% less after successive HA@ODA modification, where the hydroxyl groups of the HA enhance the water adhesion and the hydrocarbon tail of ODA provides an essential low surface energy to confer extreme water repellence, as shown in Figure 4.9E. As shown in Figure 4.9D, the

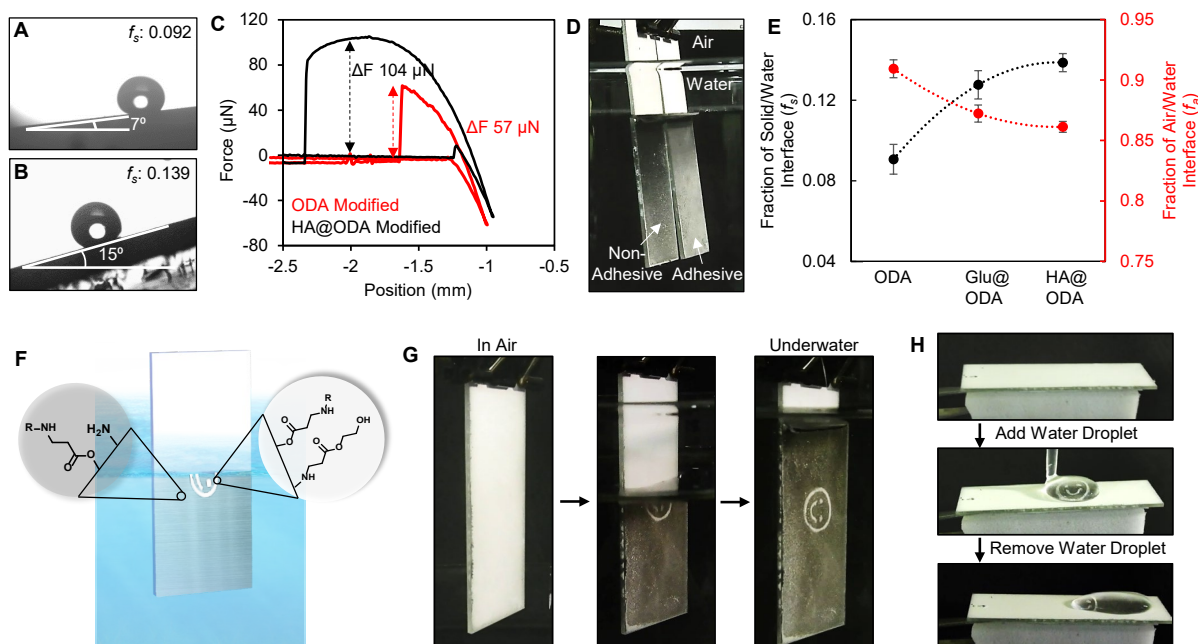


Figure 4.8 A, B) Roll-off images of a beaded water droplet on ODA modified (A) and HA@ODA modified (B) porous polymeric coatings. C) Adhesion force of a 5 μL water droplet on ODA and HA@ODA-modified adhesive coating. D) Photograph depicting the appearance of the shiny interfaces of ODA and HA@ODA-modified coatings underwater denoted as non-adhesive and adhesive, respectively. E) The fraction of contact area of the solid-beaded aqueous phase (f_s) and the air-water (f_a) interface of the porous polymeric coating after the association of selected mono-functionalization with ODA and two dual modifications of either Glu@ODA or HA@ODA. F, G) Schematic illustration (F) and corresponding photographs (G) of the appearance of an underwater smiley pattern created through strategic ODA and HA@ODA modification. H) Photographs showing the appearance of a smiley pattern of the selectively chemically modified coating upon exposure to a beaded water droplet.

trapped air in the ODA-modified coating resulted in a highly shiny appearance through the internal reflection of light after submerging the coating underwater, whereas the HA@ODA-modified coating appeared less shiny. As a result, a smiley face pattern created through spatially selective modification with HA@ODA is made visible upon exposure to water, as demonstrated in Figure 4.9F-H. These results suggest that the difference in f_a results in a distinct optical appearance of the underwater polymer coating that can be visualized with the naked eye, which agrees with previous research.⁴⁸ I note here that the smiley pattern disappears instantly upon removing it from the aqueous phase (Figure 4.9), and that this change in appearance can be repeated at least 500 times. The patterned surface also displays an outstanding ability to self-clean deposited dust particles, as shown in Figure 4.10E. To further verify the benefits of our spatially selective pattern with distinct

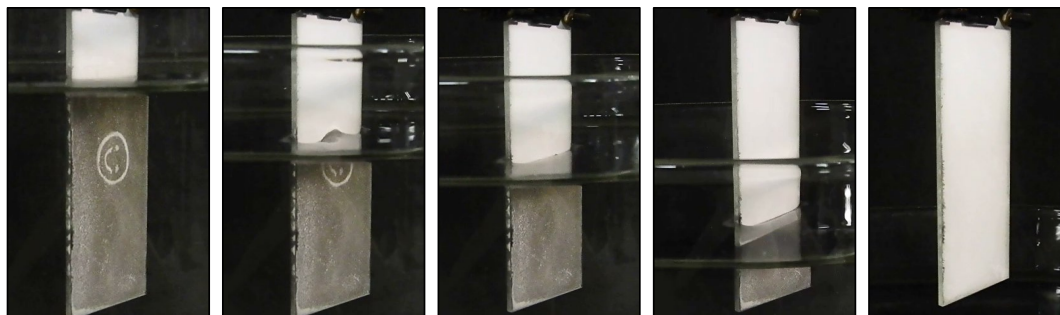


Figure 4.9 Sequential photographs revealing the immediate disappearance of the smiley patterned interface (created through spatially selective chemical modifications with HA@ ODA) when it is removed from the aqueous phase to the air.

water adhesion over two extremes of water wettability,^{35, 36} I synthesized patterned surfaces with distinct regions of superhydrophobicity and superhydrophilicity. As shown in Figure 4.10A, B, the spatial modifications of the polymeric coating with ODA and Glucamine conferred superhydrophobicity and superhydrophilicity with a water contact angle of $\sim 158^\circ$ and 0° ,

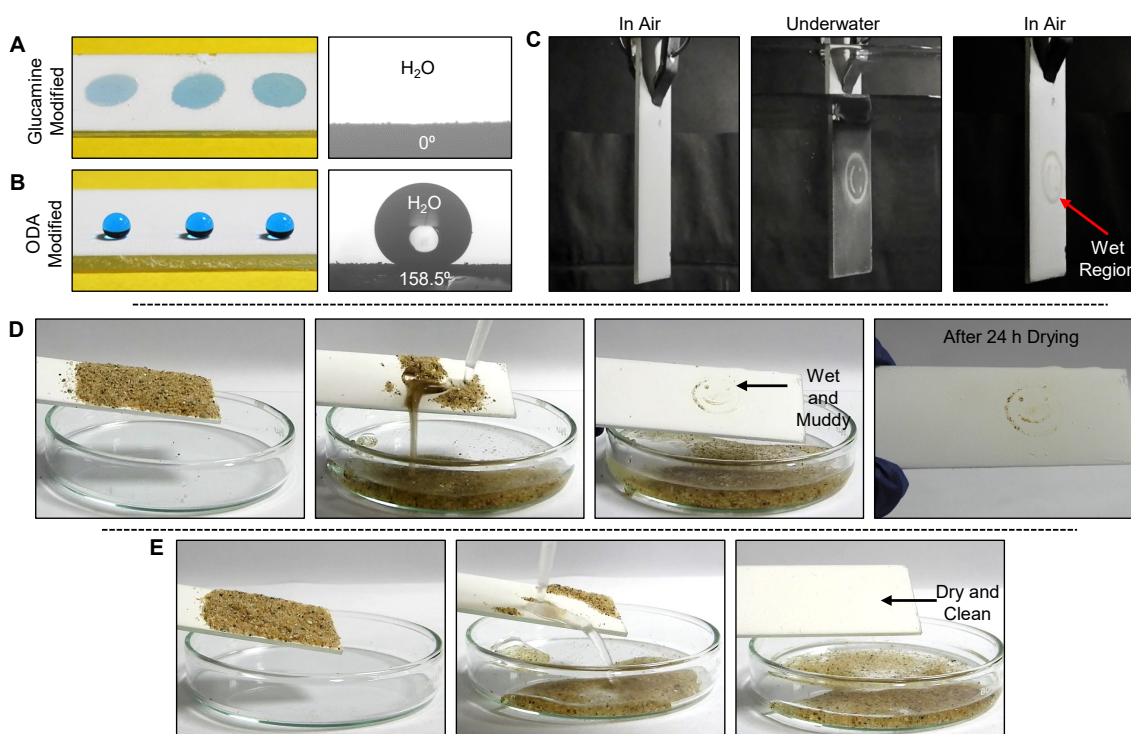


Figure 4.10 A, B) Photographs and contact angle goniometer images of beaded water droplets on glucamine (A) and ODA (B) modified coating. C) Photographs of the smiley patterned interface in the air (before submerging it), submerged, and after removing it from the water. D, E) Photographs depicting the self-cleaning performance of the smiley patterned interface developed through selective and successive chemical modifications with glucamine@ODA (D) and HA@ODA (E).

respectively. As expected, the patterned interface comprising both extremes of water wettability remained invisible in the air and visible underwater. However, the pattern remained wet after taking the surface out of the aqueous phase (Figure 4.10C), suggesting a lack of self-cleaning ability (Figure 4.10D) that is needed for real-world anti-counterfeit applications.

4.3.3. Multilevel Encryption and Orthogonal Decryption

In the final experiments, I aimed to combine the fluorescence and water adhesion characteristics into a single coating for multilevel encryption and orthogonal decryption with the naked eye. The spatially selective dual modifications of the coating with Glu and ODA (denoted as Glu@ODA)

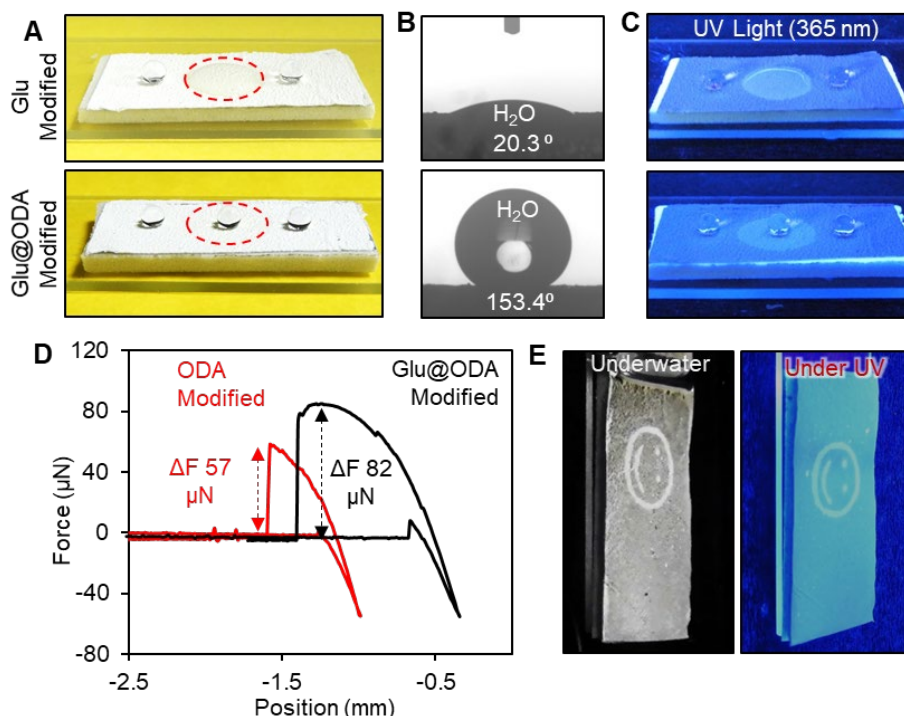


Figure 4.11 A, B) Photographs (A) and contact angle images (B) showing a superhydrophilic patterned region (Glu-modified; red dotted region) on a hydrophobic (unmodified) porous polymeric coating and a fluorescent, adhesive superhydrophobic patterned region (Glu@ODA; red dotted region) on a non-adhesive (ODA-modified) superhydrophobic polymeric coating. C) Photographs depicting the superhydrophilic fluorescent patterned region on the hydrophobic porous polymeric coating on aluminium foil that was created through selective chemical modification with Glu (red dashed region), while the dual chemical modification with Glu and ODA (red dashed region) provided an adhesive superhydrophobic fluorescent patterned region on the non-adhesive (ODA treated) region of the superhydrophobic polymeric coating. D) Adhesion force of a 5 mL water droplet on a non-adhesive (ODA-modified; red) and fluorescent, adhesive superhydrophobic coating (Glu@ODAmmodified; black). E) Photographs depicting the appearance of a smiley pattern (Glu@ODA-modified) upon submerging the polymeric coating underwater and upon irradiation with UV light (365 nm), separately.

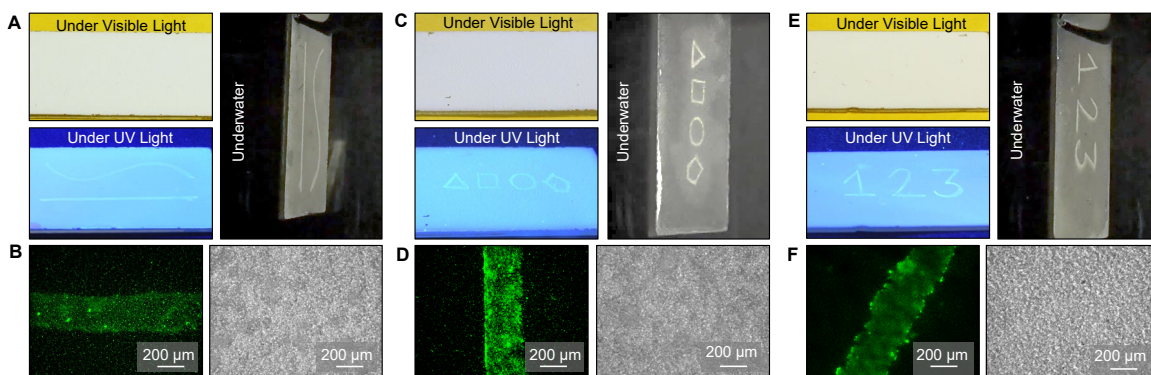


Figure 4.12 A) Photographs showing the appearance of straight- and curved-line patterns (Glu@ODA modified) of micrometre-sized width upon submerging the coating underwater and under UV light illumination, separately. B) Fluorescence and bright field microscope images of straight-line patterned region of the polymeric coating. C) Photographs showing the appearance of different geometrical patterns (Glu@ODA modified) including triangle, square, circle, and pentagon of micrometre-sized width upon submerging the coating underwater and under UV light illumination, separately. D) Fluorescence and bright field microscope images of the square patterned region of the polymeric coating. E) Photographs showing the appearance of numbers (Glu@ODA modified) including 1, 2, and 3 of micrometre-sized width upon submerging the coating underwater and under UV light illumination, separately. F) Fluorescence and bright field microscope images of the number 2 patterned region of the polymeric coating.

conferred both fluorescence and adhesive superhydrophobicity (Figure 4.11A-C). As demonstrated in Figure 4.11D, the adhesion force experienced by a beaded water droplet on the Glu@ODA modified interface was around 50% higher (82 mN, black line) than the ODA-modified interface (57 mN, red line). This spatially selective modulation of the porous polymeric coating with Glu and ODA allowed the co-association of water adhesion and UV responsiveness in the same location, as shown in Figure 4.11C. For example, a smiley face pattern that is invisible under visible light in the air can be read when the surface is submerged underwater or when it is exposed to UV light, as shown in Figure 4.10E. In addition to the smiley pattern, the simplicity of this

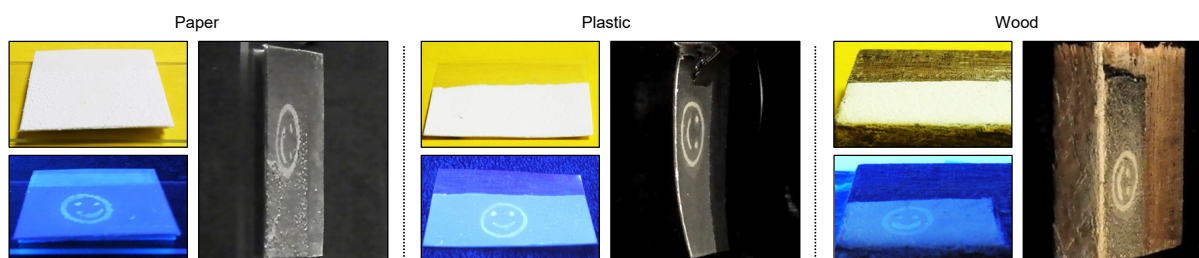


Figure 4.13 Photographs showing the polymeric coating on different substrates and the appearance of a smiley pattern upon exposure to water and UV light, separately.

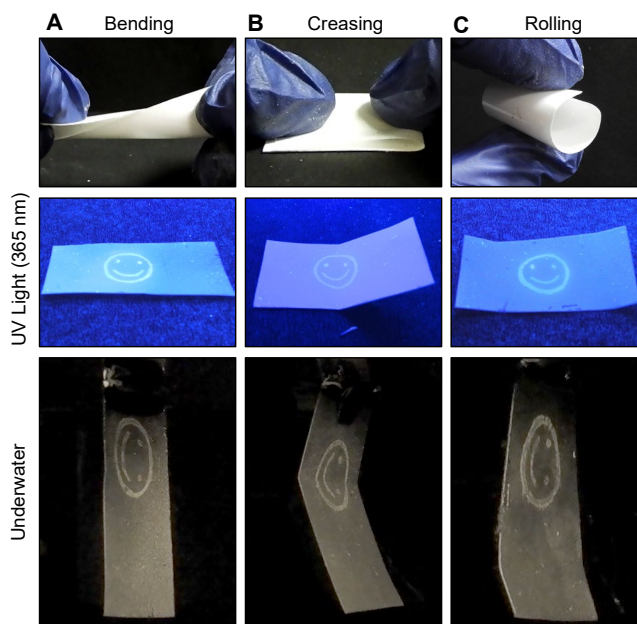


Figure 4.14. Photographs showing the effect of bending, creasing, and rolling on the smiley patterned coating on a flexible plastic substrate.

method allowed the creation of various patterns of micrometre-sized width such as geometric patterns (straight line, curved line, triangle, square, circle, pentagon), numbers, etc. (Figure 4.12A-F). This coating can be applied to various flexible and rigid substrates, including aluminium foil, plastic, paper, and wood (Figure 4.13), and the water wettability and fluorescence remained intact even after bending, creasing, and rolling the coating on a flexible substrate multiple time (Figure 4.14A-C). the appearance and performance of the coating also remained unaltered even after

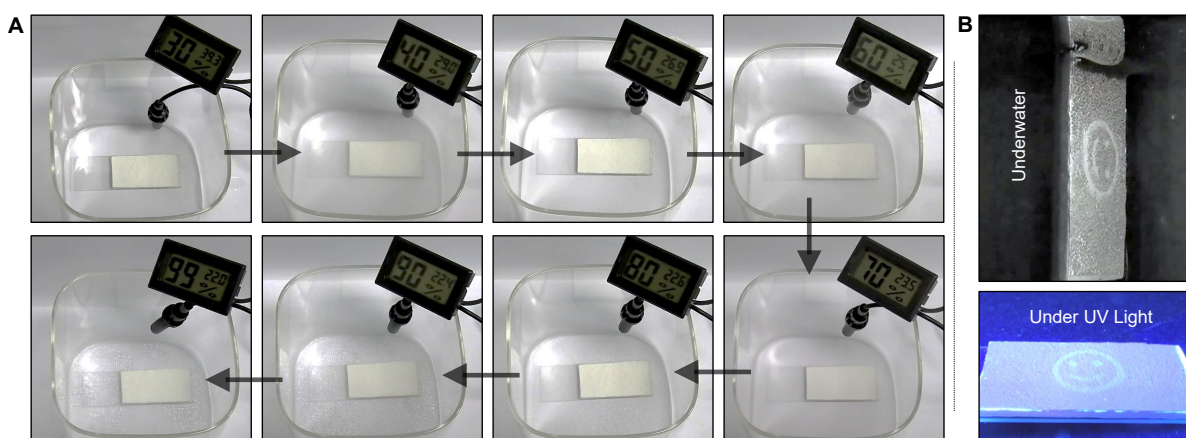


Figure 4.15. A) Photographs demonstrating the effect of different relative humidity on Glu@ODA modified smiley patterned polymeric coating. B) Photographs showing the appearance of a smiley pattern both underwater and under UV light after exposing the polymeric coating to different relative humidity.

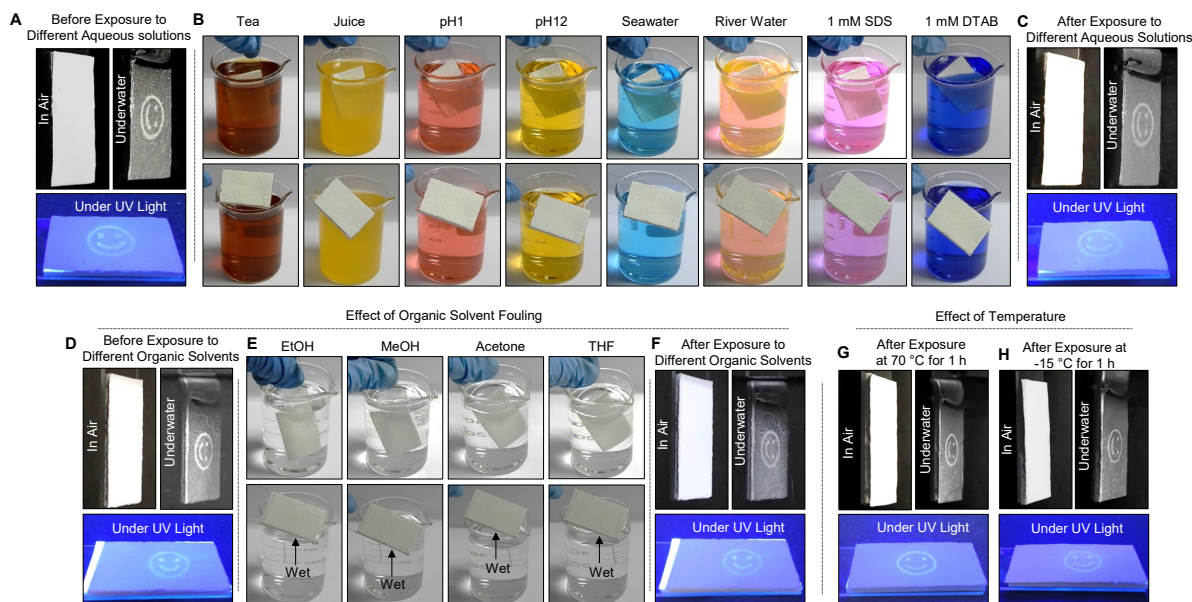


Figure 4.16. A) Photographs showing the appearance of a smiley pattern (Glu@ODA modified) upon submerging the coating underwater and upon irradiation with UV light, separately before exposure to different contaminated aqueous solutions. B) Photographs demonstrating the results of dipping the Glu@ODA patterned polymeric coating in various aqueous solutions, including tea, juice, pH 1, pH 12, saltwater, river water, 1 mM SDS, and 1 mM DTAB. C) Photographs showing the appearance of a smiley pattern (Glu@ODA modified) upon submerging the coating underwater and upon irradiation with UV light, separately even after exposure to these different contaminated aqueous solutions. D) Photographs showing the appearance of a smiley pattern (Glu@ODA modified) upon submerging the coating underwater and upon irradiation with UV light, separately before exposure to different organic solvents. E) Photographs demonstrating the wetting of Glu@ODA patterned polymeric coating after dipping in ethanol (EtOH), methanol (MeOH), acetone, and tetrahydrofuran (THF). F) Photographs showing the appearance of a smiley pattern (Glu@ODA modified) upon submerging the coating underwater and upon irradiation with UV light, separately even after exposure to different organic solvents. G, H) Photographs showing the appearance of a smiley pattern (Glu@ODA modified) upon submerging the coating underwater and upon irradiation with UV light, separately even after exposure to extreme temperatures for 1h including 70 °C (G) and -15 °C (H).

exposure to various humid environments (Figure 4.15A, B) and the pattern remained invisible even at 99% humidity, compared to previous reports of superhydrophobic–superhydrophilic patterned interfaces.³⁵ In addition, when exposed to various contaminated aqueous phases, such as tea, juice, pH1, pH12, river water, ocean, and surfactant-contaminated (1 mM SDS and 1 mM DTAB) water, the Glu@ODA-modified patterned surface remained dry and the appearance of the pattern remained consistent both underwater and when illuminated with UV light, as shown in Figure 4.16A-C. Moreover, due to the covalent immobilization of Glu and ODA on the polymeric coating,

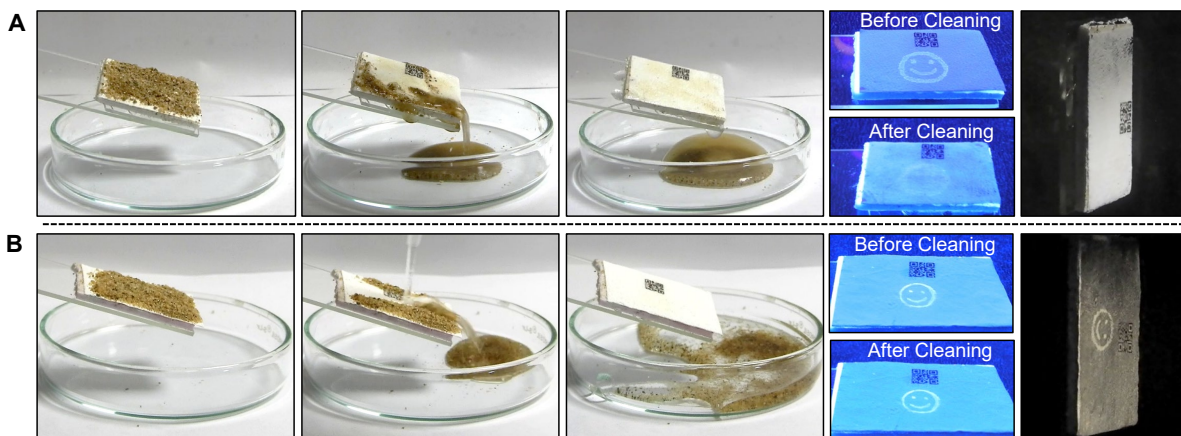


Figure 4.17. A, B) Photographs comparing the self-cleaning performance of the deposited dust particles on the smiley patterned interface after Glu modification (A) and dual chemical modifications with Glu@ODA (B).

the appearance of the smiley pattern was maintained even after immersion in various organic solvents (Figure 4.16D-F). Furthermore, the anti-counterfeiting performance remained unaffected even at extreme temperatures (70 °C and -15 °C), as shown in Figure 4.16G, H. In contrast to only Glu patterned interface, the Glu@ODA-modified interface maintained its self-cleaning ability (Figure 4.17A, B and Figure 4.18A, B). As a proof-of-concept for multilevel anticounterfeiting applications, I demonstrated the facile and orthogonal authentication of quick response (QR) codes using the chemically modulated smiley pattern. As shown in Figure 4.19A, three flexible aluminum foil strips were coated with our polymeric coating, each with a different set of chemical modifications (ODA, patterned HA@ODA, and patterned Glu@ODA for Interfaces 1, 2, and 3,

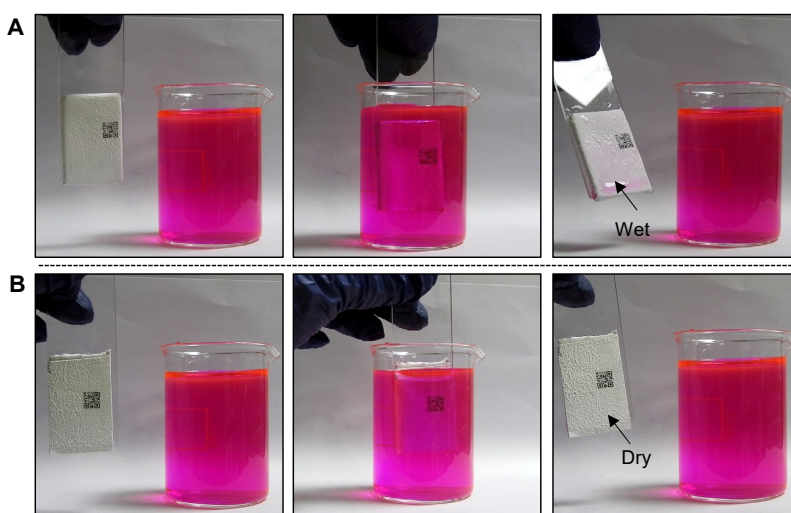


Figure 4.18. A, B) Photographs depicting the effect of dyed (Rhodamine B) aqueous exposure on the smiley patterned interface after Glu modification (A) and after dual chemical modifications with Glu@ODA (B).

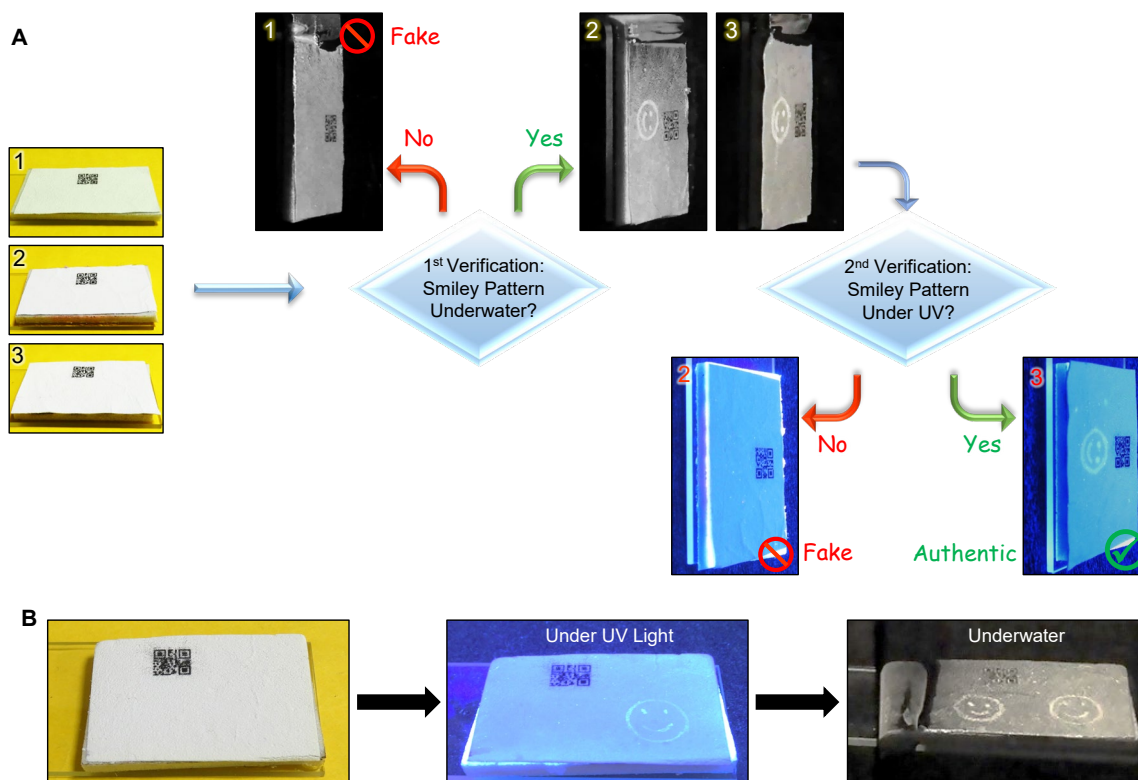


Figure 4.19. A) Flow chart demonstration to identify the authentic QR code based on the appearance of a smiley pattern both underwater and under UV illumination. B) Photographs to demonstrate authenticity of a QR code, two distinct smiley patterns were embedded, where one and two smiley faces were appeared in 1st and 2nd verification steps, respectively.

respectively). Then, a QR code was printed on each interface. In the first authentication step, all three interfaces, with identical QR codes, were submerged in water to visualize the smiley face pattern. Interfaces 2 and 3 showed the smiley face, whereas Interface 1 only showed a uniform shiny surface. In the second verification step, the same smiley face appeared under UV light on Interface 3 but not on Interface 2. These results suggest that only Interface 3 is identified as authentic. In addition, inspired by the earlier demonstrations,^{52–54} here these two distinct smiley faces were embedded next to a QR code prior to examining them in two different verification steps, i.e. under UV light (1st verification) and underwater (2nd verification). I noticed that one smiley face appeared on exposure to UV light—but two distinct smiley faces appeared underwater as shown in Figure 4.19B. Thus, these simple two-step verifications validated the authenticity of the QR code unambiguously. In the past, superhydrophobic/superhydrophilic pattern interfaces have been explored in various different applications.^{35,36,55–71} However, the strategic design of absolutely self-cleanable and water-repellent pattern consisting of adhesive and non-adhesive

superhydrophobicity is unprecedented—and such an approach provided superior anticounterfeiting performance.^{35,36,55-71} In the past, few reports introduced the pattern of extremes of water wettability—i.e. superhydrophilicity and superhydrophobicity in anticounterfeiting application, where the selective and instant infiltration of water in hydrophilic domains caused an essential change in optical transparency—but such earlier reported pattern remained visible till the infiltrated water get evaporated from the patterned interface. Moreover, the superhydrophilic/superhydrophobic patterns inherently remained inappropriate to self-clean deposited dust/ dirt as demonstrated in Figure 4.10D.

4.4 Conclusions

In summary, I reported the design and synthesis of physically unclonable coatings that enable multilevel anticounterfeiting by chemical and spatial modification. Notably, the encryption can be independently authenticated by following one or both, an automated machine learning process and an instrument free, naked-eye readout technique. Furthermore, this class of coatings can be applied to a wide range of substrates and are resistant to aqueous exposures and other contaminations that are common in real-world environments. Overall, this strategic association of water adhesion and fluorescence on an extremely water repellent interface allowed the development of self-cleanable coatings with physically unclonable features for an orthogonal and multilevel readout of authenticity.

4.5 References

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Chapter 5: Designing a Network of Crystalline Polymers for a Scalable, Nonfluorinated, Healable and Amphiphobic Solid Slippery Interface

The fluorinated-liquid infused amphiphobic slippery interfaces exhibiting superior sliding of the beaded oil/water droplets, often suffer from durability and contamination issues. Here, the ability of 1) hexagonal packing of hydrocarbon sides in a selected “comb-like” polymer and 2) its reversible phase transition at 51°C was rationally exploited to achieve temperature-assisted rapid (<1 minute) and repetitive (50 times) self-healable amphiphobic solid-slippery coating on both planar and geometrically-complex substrates. The selected “comb-like” polymer was strategically infused in a porous, hydrophilic, and thick ($\approx 4.8 \mu\text{m}$) polymeric coating. The resultant solid and smooth interface exhibited sliding of beaded droplets of various liquids, including droplets of water, polar (ethanol, 1-propanol, 1-hexanol, DMSO, DMF), and non-polar (decane, dodecane, diiodomethane) organic solvents, edible (vegetable oil), motor, engine (petrol, diesel, kerosene) and crude oils.

M. Dhar, A. Das, D. Parbat and U. Manna, *Angew. Chem. Int. Ed.*, 2022, **61**, e202116763.

5.1 Introduction

Designs of different bio-inspired homogeneous and heterogeneous liquids wettability that allow spontaneous rolling or sliding of beaded water/oily phases remain an elegant approach to develop various and prospective functional materials related to the environment, energy, and biomedical applications.¹⁻¹⁷ Unfortunately, the heterogeneous super-liquid wettability in air often failed to survive under harsh (elevated temperature and pressure) and abrasive (physical and chemical) conditions—due to the delicate nature of the external and metastable third phase (i.e., cushion of trapped air in a textured interface).^{2,18-19} To combat this common and vital challenge, ultra-smooth and homogeneous slippery interfaces were introduced following a few distinct and innovative approaches.^{2-4,7-8,13,15-17} Aizenberg and co-workers introduced a seminal report on nepenthes pitcher plant inspired omniphobic slippery liquid infused porous surface (SLIPS) through the strategic infusion of fluorinated liquid lubricant in an appropriately decorated porous and featured interface.² The infused liquid lubricant in the textured interface provided a defect-free, ultra-smooth, and wet slippery property—and the fluidity of the infused liquid lubricant provided the much needed self-repairing ability to the physically damaged interfaces.² But, at the same time, the unavoidable leaching of infused liquid lubricant from such wet slippery interfaces severely a) affects the durability of the bio-inspired wettability—and b) contaminates the beaded probe liquids.²⁰⁻²²

In contrast to these earlier approaches, various research groups strategically and independently exploited poly(dimethylsiloxane) (PDMS) to achieve a covalently attached, ultra-smooth and thin solid and dry slippery interface—without i) associating any featured interface and ii) lubrication of fluorinated liquid.^{3-4,7-8,13,15} Such a non-fluorinated and environmentally viable approach successfully provided an optically transparent solid slippery interface towards beaded droplets of water, other polar solvents, and alkanes.^{3-4,7-8,13,15} But, the sliding of inherently complex liquid—i.e., crude oil and commercially available various refined oils is yet to demonstrate on such solid slippery interfaces. Moreover, such covalently attached and liquid lubrication-free slippery coating remained inappropriate for self-repairing the physical damages and remained less appropriate to withstand even practically relevant severe other conditions such as prolonged exposure to extremes of pH and UV-light.²³⁻²⁴

Very recently, Tiwari and co-workers introduced a distinct approach for developing a robust and transparent amphiphobic solid slippery surface, where a thin hierarchical surface (~ 200 nm) fabricated with metal–organic framework (MOF) slides the beaded droplets of water and

vegetable oil on the tilted (15°) interface.¹⁷ While such an approach is fundamentally interesting, the laborious and time-consuming layer-by-layer surface growth of MOF at autoclave condition (120 °C) appeared as a major challenge.¹⁷ Moreover, the Zirconium-based MOFs are known for their limited stability at highly alkaline condition.²⁵ Such MOF-based slippery coating is also remained inappropriate to self-repair the physical damages.

In another approach, the paraffin wax that displays a temperature-dependent reversible phase transition was strategically associated for developing thermo-responsive, patterned, and temperature-assisted self-healable solid slippery interfaces.²⁶⁻²⁸ Beaded droplets of mainly

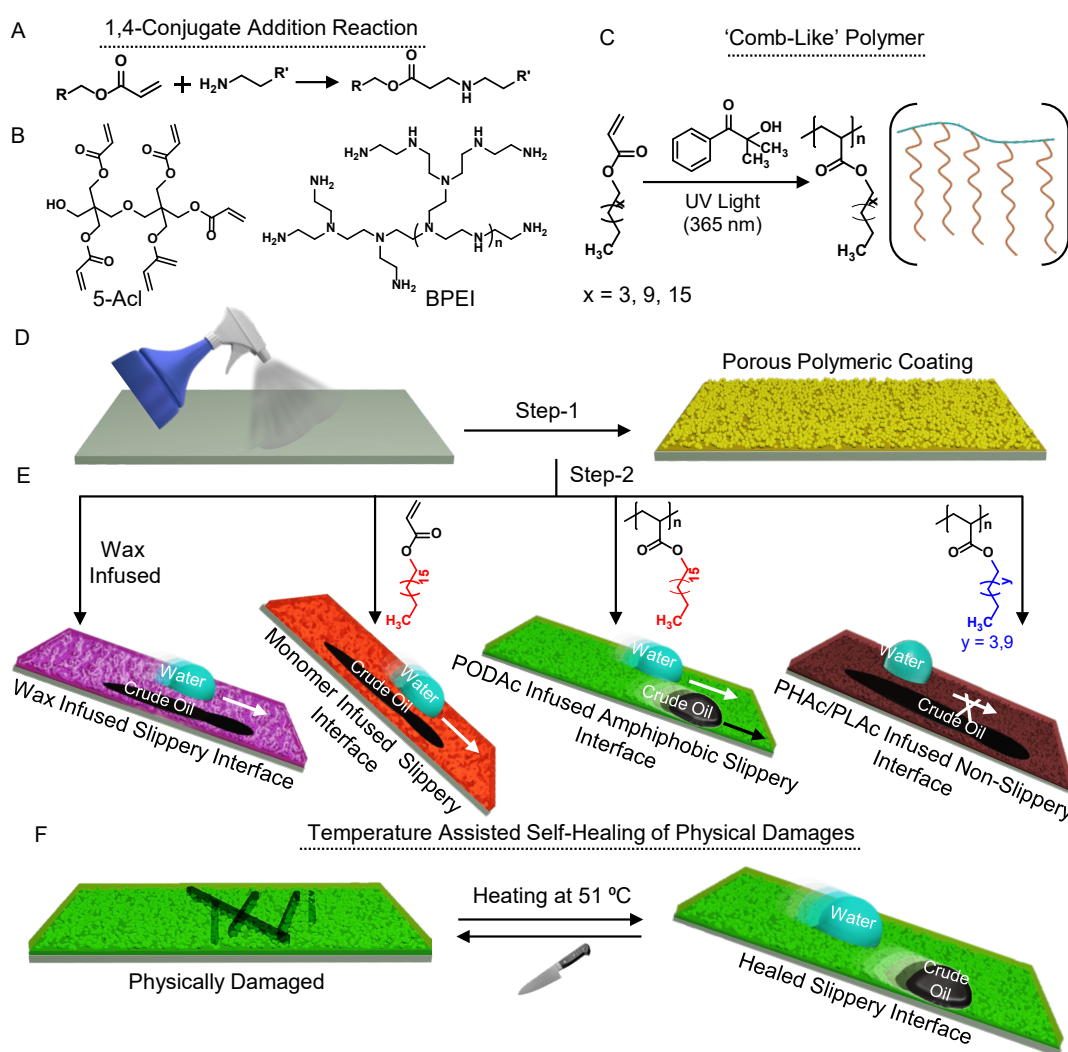


Figure 5.1 A) Schematic presentation of 1,4-conjugate addition reaction between amine and acrylate functional groups. B) Chemical structure of dipentaerythritol penta-acrylate (5-Acl) and branched polyethyl enamine (BPEI). C) Schematic illustration of photopolymerization of octadecyl acrylate monomer (ODA) to 'comb-like' polymer polyoctadecyl acrylate (PODAc) in presence of a radical. D-E) Schematic diagram illustrating the two-step fabrication procedure of different slippery coatings. F) Schematic illustrating the temperature assisted self-healing of physically damaged amphiphobic solid slippery coating.

polar solvents of different surface tensions (i. e., water, DMSO, ionic liquid, formamide, etc.) can easily slide on such surfaces.²⁶⁻²⁸ But, the association of a fluorinated nano-structure with the paraffin wax is required to slide both the beaded droplets of water and a non-polar organic solvent, i.e., hexadecane.¹⁶ Overall, the demonstrations of sliding the beaded droplets of engine, motor, edible, and inherently complex crude oils on the earlier reported non-fluorinated solid slippery interfaces are extremely rare.^{3-4, 7-8, 13, 15, 16, 17, 26-28} Hence, further designs are required for facile and scalable fabrication of a non-fluorinated, highly scalable, and self-healable solid amphiphobic slippery coating—that would slide a wide range of beaded liquid droplets of polar (water, ethanol, DMF, DMSO) and non-polar solvents (decane, dodecane, diiodomethane, etc.) as well as more relevant and realistic non-polar liquids—including engine oils (diesel, kerosene, petrol), edible oil (vegetable oil) and crude oil (a highly complex non-polar liquid).

Here, I report a non-fluorinated, substrate-independent, and self-healable amphiphobic solid slippery coating following a simple and scalable fabrication process. The strategic use of 1,4-conjugate addition reaction between selected reactants (polyethylenimine, branched (BPEI; Mw ~ 800 Da) and dipentaerythritol penta-acrylate (5-AcI)) provided porous polymeric coating to infuse selected lubricant—i.e, ‘comb-like’ polymer having variable hydrocarbon side chain as shown in Figure 5.1. The strategic utilization of the crystallinity and the thermo-responsive phase transition properties of the selected ‘comb-like’ polymer yielded a self-healable and amphiphobic solid-slippery interface through the association of crystalline network. The performance of ‘comb-like’ polymer infused solid-slippery interface is compared with paraffin wax and octadecyl acrylate (ODAc) monomer infused solid-slippery interfaces (see Scheme 5.1E).

5.2 Experimental Section

5.2.1 Materials Required

2-hydroxy-2-methylpropiophenone, decane, dodecane, diiodomethane, and paraffin wax were purchased from Sigma Aldrich (Bangalore, India). Dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) were purchased from Alfa-Aesar, India. Crude Oil was obtained from Oil India Refinery, Assam. Vegetable oil and spray bottle was purchased from Amazon, India. Honey and mobile safety covers were purchased from a local chemical shop. Details of other chemicals used in this work are provided in Chapter 2.

5.2.2 Characterization

Atomic force microscope (AFM) images were acquired using OXFORD Cypher Atomic Force Microscope. X-ray diffraction measurement was done using a Rigaku Smartlab X-ray diffractometer with copper K α ($\lambda=1.54$ Å) as a source with 9 kW power. The transition temperature was measured using a differential scanning calorimeter (Mettler Toledo DSC1) under nitrogen atmosphere. NMR spectra were recorded using Bruker 500 MHz NMR spectrometer. Other characterization details are provided in Chapter 2.

5.2.3 Preparation of Different Acrylate Polymers

All acrylate polymers were synthesized through the photopolymerization process. First, 10 g of acrylate monomer was dissolved in 15 mL of ethanol, and 50 μ L of 2-hydroxy-2-methylpropiophenone initiator was added to the prepared ethanolic solution of acrylate monomer. Next, this solution was kept under UV irradiation of 365 nm wavelength for photopolymerization. After 30 min, the phase-separated polymers were collected and reprecipitated from THF into ethanol. Polyoctadecyl acrylate (PODAc) was retrieved as a white powder, whereas poly lauryl acrylate (PLAc) and poly hexyl acrylate (PHAc) appeared as viscous liquids.

5.2.4 Fabrication of Amphiphobic Solid Slippery Coating

The fabrication procedure involves the preparation of porous matrix followed by infusion of PODAc. In the first step, the porous polymeric matrix was prepared by simple spray deposition technique using a commercially available spray bottle. First, solutions of 5-Acl (0.1325 g/mL) and BPEI (0.05 g/mL) were prepared in hexanol. Then 10 mL of 5-Acl solution was mixed with 3 mL of BPEI solution, and the reaction mixture was kept under vigorous agitation for 1 min. Next, this solution was sprayed manually from a 10 cm distance over an area of 200 cm². After spray deposition, the substrates were kept under open air for 10 min. Then, the substrates were washed with THF and dried in the open air. The second step involves the infusion of PODAc. 30 mg of PODAc was dissolved in 2 mL of THF, and from there, 200 μ L of the solution was infused in 7.5 cm $\times$ 2.5 cm area of the prepared porous matrix. After infusion, the coating was kept in an oven at 70 °C for 5 minutes to dry out the THF before cooling down to room temperature. Other coatings mentioned in this work were prepared following the same procedure mentioned in the above section. For PLAc and PHAc infused coating, 240 mg of each polymer was dissolved in 2 mL of THF and 200 μ L of the solution was deposited on 7.5

cm $\times$ 2.5 cm area of the porous matrix. For wax-infused coating, 122 mg of melted paraffin wax was directly infused over an area of 7.5 cm $\times$ 2.5 cm of the porous matrix. ODAc monomer infused coating was prepared by directly infusing the melted ODAc in the porous matrix followed by cooling down to room temperature.

5.2.5 Chemical and Physical Durability Tests

Different chemical and physical durability tests were performed on PODAc infused amphiphobic solid slippery coating. The detailed procedure of these durability tests was explained in the following section.

5.2.5.1 Chemical Durability Tests

The amphiphobic solid slippery interface was subjected to various chemical exposures—including artificial seawater (MgCl₂ (0.226g), MgSO₄ (0.325g), NaCl (2.673g), and CaCl₂ (0.112g) in 100 mL of deionized water), river water, extremes of pH (2 and 12), surfactant (SDS solution (1mM), DTAB solution (1 mM)) and UV irradiation (254 nm and 365 nm). The slippery property of the coating remained unaltered even after 15 days of continuous exposure, which was confirmed by sliding angle measurements with four different liquids, including water, crude oil, petrol and ethanol.

5.2.5.2 Physical Durability Tests

a) Sand Paper Abrasion

400 grit abrasive sandpaper (1 cm $\times$ 2 cm) was rubbed manually in a back-and-forth motion across the PODAc-infused coating with an applied pressure of 6 KPa for about a distance of 200 cm. Next, the physically damaged coating was heated at a high temperature with the help of a hairdryer and cooled down to room temperature. Then, the slippery property of the coating was examined through sliding angle measurements with two different liquids, including water and ethanol.

b) Adhesive-tape Peeling Test

An adhesive tape was attached to the surface of the PODAc-infused coating with an applied load of 500 g for homogeneous contact between the surface and load. Then the adhesive tape was detached manually from the surface of the coating. This procedure was repeated 20 times. Then, the slippery property of the coating was examined through sliding angle measurements.

5.3 Results and Discussions

5.3.1 Development of Amphiphobic Solid Slippery Interface

In the current design, firstly, a thick ($4.86\ \mu\text{m}$) and porous polymeric coating was developed through a 1,4-conjugate addition reaction between amine and acrylates by the spray depositing the reaction mixture of BPEI and 5-Acl at ambient conditions as shown in Figure 5.1D. The highly porous features (Figure 5.2A) in the prepared polymeric coating provided an adequate space to hold selected phase transitioning lubricants. The prepared porous polymeric coating was found to be inherently hydrophilic and superoleophilic—where the droplets of water and crude oil beaded with contact angles of $\sim 56^\circ$ and 0° , respectively (Figure 5.2B-E). Secondly, the prepared porous polymeric coating was infused with selected lubricants—including paraffin wax and different ‘comb-like’ polymers to compare the associated different types of solid slippery properties. The infusion of paraffin wax ($6.5\ \text{mg}/\text{cm}^2$) in the as-prepared hydrophilic and porous polymeric coating without any further chemical modifications, unlike the previous reports, provided an optically translucent (transparency below 20 %, see Figure 5.2F) solid slippery coating. The beaded droplets of water and different organic polar solvents (Ethanol, 1-propanol, DMF, and DMSO) with various surface tensions readily slide on this coating on tilting the surface at 15° . However, the droplets of non-polar solvents (i.e., decane, dodecane), crude oil, and various commercially available refined oils (including vegetable oils, motor oil, kerosene, petrol, diesel etc.) failed to slide from the same slippery surface as shown in Table 5.1. On the other hand, the infusion of a selected and crystalline (Figure 5.5A) “comb-

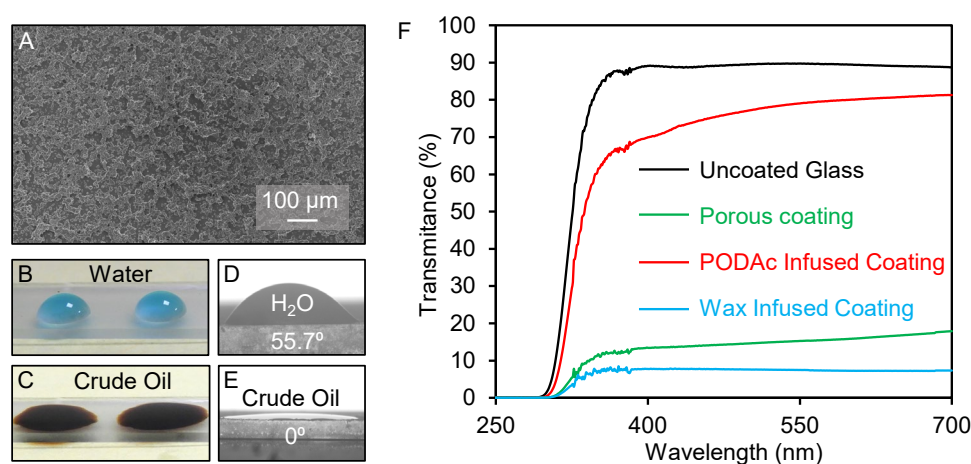


Figure. 5.2 A) FESEM images of porous polymeric coating. B,C) Digital images of beaded droplet ($10\ \mu\text{L}$) of water (B) and crude oil (C) on porous polymeric coating. D,E) Static contact angle images of a beaded droplet ($4\ \mu\text{L}$) of water and crude oil on porous polymeric coating. F) Optical transmittance spectra of bare glass slide (black), PODAc infused coating (red), porous polymeric coating (green), wax infused coating.

		PODAc infused	Wax infused
	Liquids	SA (°)	SA (°)
Non polar Organic solvents	Decane	8	×
	Dodecane	8	×
	Diiodomethane	8	8
Non-polar Refined and complex oils	Motor oil	15	×
	Veg oil	15	×
	Crude oil	15	×
	Petrol	8	×
	Diesel	8	×
	Kerosene	8	×
Polar solvents	Ethanol	12	15
	1-Propanol	12	15
	1-Hexanol	15	×
	DMF	12	15
	DMSO	12	15
	Water	15	15

Table 5.1 Table showing the sliding angle values for different polar and non-polar liquids on PODAc and wax infused coating.

like” polymer (i.e., poly(octadecyl acrylate) (PODAc), $M_n \approx 98600$ Da; Figure 5.3 and Figure 5.4) in the same porous polymeric coating resulted in a highly efficient amphiphobic solid-slippy interface with significantly improved optical transparency (80%, Figure 5.2F). The spontaneous sliding of both the beaded droplets of water (volume of 30 μ L) and crude oil (volume of 10 μ L) with a sliding angle (SA) of 15° was noted on the “comb-like” polymer

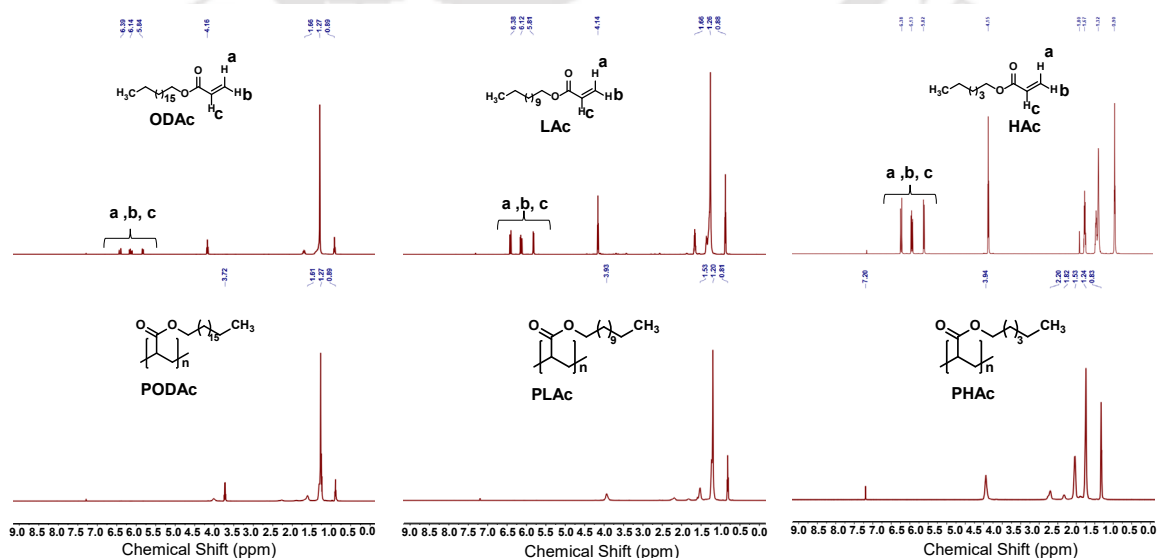


Figure 5.3 NMR spectra of ODAc, LAc, HAc, PODAc, PLAc, PHAc.

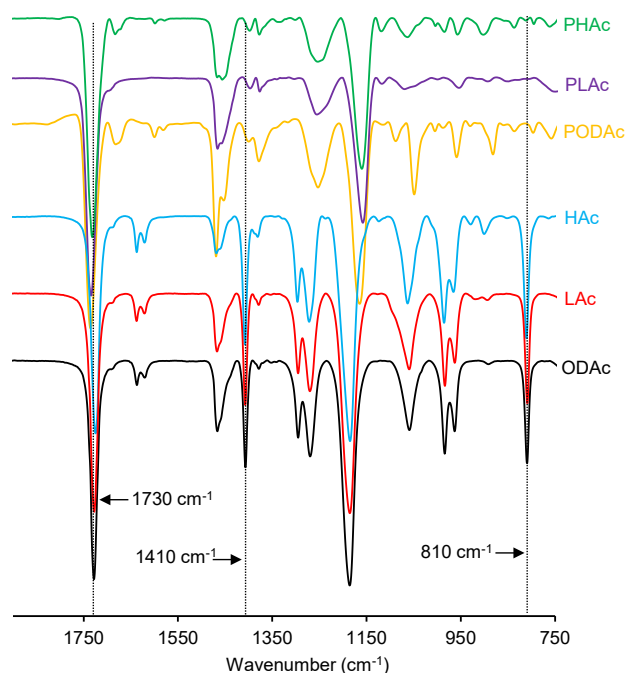


Figure 5.4 FTIR-ATR spectra of ODAc (black), LAc (red), HAc (blue), PODAc (yellow), PLAc (purple), PHAc (green). The successful photopolymerization was confirmed by the significant depletion of 1410 cm^{-1} peak corresponding to C–H deformation of the β -carbon of the vinyl group with respect to carbonyl stretching peak at 1730 cm^{-1} . Also, decrease of the peak at 810 cm^{-1} assigned to $=\text{CH}_2$ confirms the polymerization of acrylate monomers.

infused coating as shown in Figure 5.5A. But, the loading amount of the “comb-like” polymer displayed a significant influence on the slippery property. The gradual increase in the loading amount of PODAc (from 0.27 mg/cm^2 to 3.2 mg/cm^2) improved the slippery property significantly, as shown in Figure 5.5B. While the porous and hydrophilic polymeric coating with PODAc loading of 0.27 mg/cm^2 failed to provide any slippery property, the enhancement of the loading amount of PODAc to 1.6 mg/cm^2 yielded an amphiphobic solid-slippery interface where the beaded droplets of crude oil and water readily slide off as shown in Figure 5.5B. It is worth mentioning that the static water contact angle (WCA) was gradually increased from $\sim 56^\circ$ to $\sim 107^\circ$ on increasing the amount of infused PODAc to 1.6 mg/cm^2 , but no further change in WCA was noticed beyond this loading amount of PODAc, as shown in Figure 5.5C. At lower PODAc concentrations, the incomplete coverage of the underlying hydrophilic porous matrix resulted in lower water static contact angles. However, gradually increasing the amount of infused polymer PODAc resulted in enhanced coverage of the underneath porous matrix, thereby gradually increasing the water static contact angle. The porous coating was completely covered by the infused PODAc at a PODAc concentration of 1.6 mg/cm^2 and reached the lowest possible surface free energy. Consequently, further increasing the PODAc concentration did

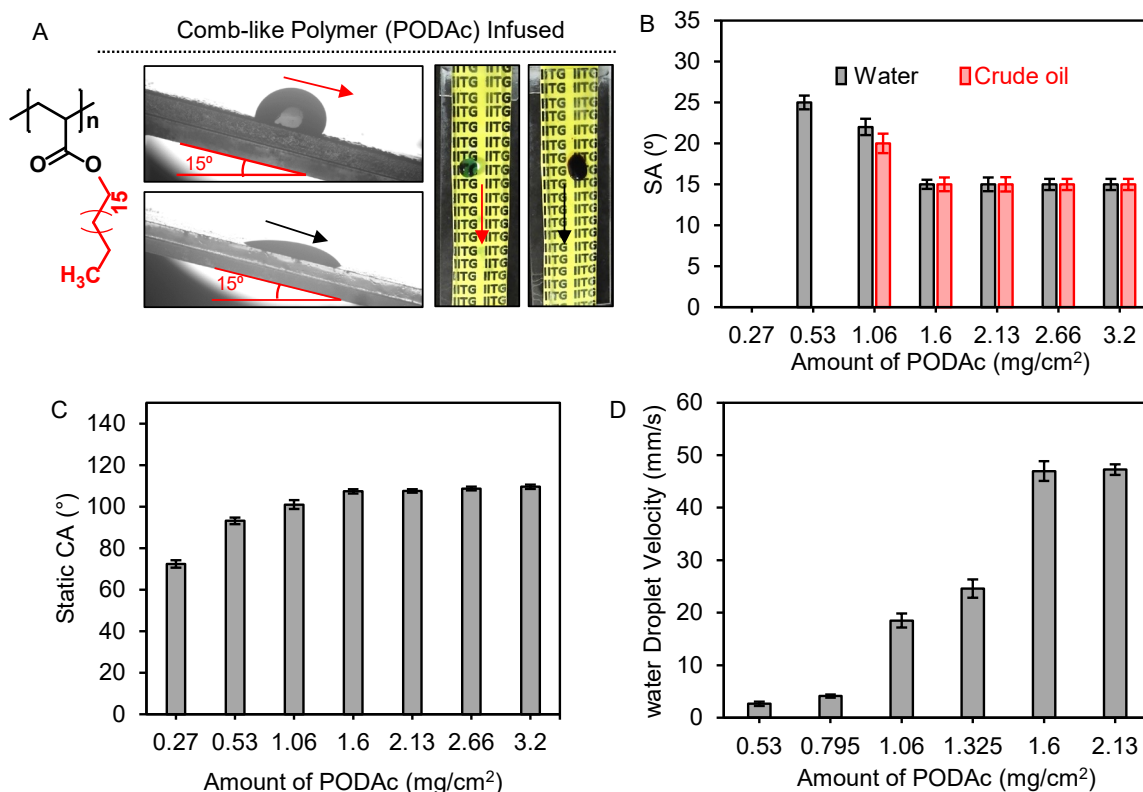


Figure 5.5 A) Sliding angle and digital images of the PODAc infused coating showing the sliding of both water and crude oil. B) Bar diagram accounting the sliding angles of water and crude oil on PODAc infused coating upon changing the amount of infused PODAc. C) Bar diagram illustrating the change in the static water contact angles on increasing the loading amount of infused PODAc in the porous polymeric coating. D) Bar diagram accounting for the velocity of beaded water droplet (30 μL) at a fixed tilting angle (25°) upon increasing the loading amount of the infused PODAc in the porous polymeric coating.

not influence the water wettability, and the static contact angle of the water droplet remained similar beyond the 1.6 mg/cm^2 concentration of PODAc. Interestingly, on increasing the loading amount of PODAc, a significant increment ($\approx 2.6 \text{ mm s}^{-1}$ to $\approx 47 \text{ mm s}^{-1}$) in the velocity of beaded water droplet (30 μL) was noted at a fixed sliding angle of 25° (Figure 5.5D). The elevated velocity of the beaded droplet of water indicates the improved slipperiness in the prepared solid slippery interface.²⁹ Eventually, this simple chemical approach provided a facile basis to regulate the surface slipperiness. The solid slippery property also depended on the choice of comb-like polymers. Interestingly, the same porous polymer coating infused with other “comb-like” polymers having shorter hydrocarbon side chains, including poly(hexa acrylate) (PHAc) and poly(lauryl acrylate) (PLAc), absolutely failed to provide slippery coating, even on increasing the loading amount to 12 mg/cm^2 , rather the beaded droplets of water and crude oil were pinned (at 90° tilting angle) and spilled, respectively, as shown on Figure 5.6A, B. Further, the X-ray diffraction (XRD) pattern and cross-polarized light

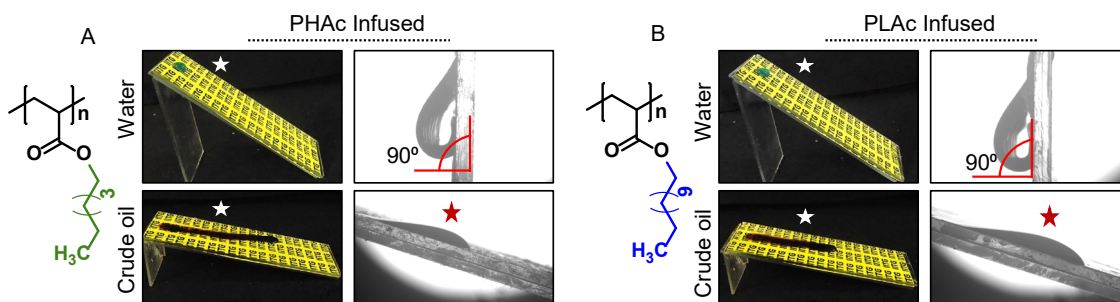


Figure 5.6 A,B) Digital images and contact angle images demonstrating the pinning and spilling of beaded water and crude oil droplets, respectively, on the PHAc (A) and PLAc (B) infused coating.

microscope images were analyzed to understand such differences in slippery properties for different comb-like polymers. The PODAc infused porous polymeric coating displayed an X-ray diffraction peak (at 2θ of 22.08°) corresponding to the hexagonal packing with a spacing of $4.02 \text{ \AA}$, which resembled the crystalline α phase (hexagonal packing) of respective monomer (ODAc, Figure 5.7A).³⁰ The octadecyl side group of the infused PODAc in the porous polymeric coating followed a hexagonal packing, which eventually provided a crystalline network in the porous polymeric matrix, whereas no such sharp XRD peak was noted for other comb-like polymer (PHAc, PLAc) infused porous polymeric coatings, as shown in Figure 5.7A. Thereafter, the appearance of uniform birefringence under a cross-polarized light microscope reconfirmed the presence of a continuous crystalline network in the PODAc infused porous polymeric coating, as shown in Figure 5.7B. However, no such birefringence appeared for the same porous polymeric coating infused with either PHAc or PLAc (Figure 5.7C, D). Thus, the “comb-like” polymers with shorter hydrocarbon side groups that failed to provide a crystalline network in the porous polymeric coating, did not exhibit sliding behaviour for the beaded droplets of water and crude oil. Further, the infusion of octadecylacrylate (ODAc), the

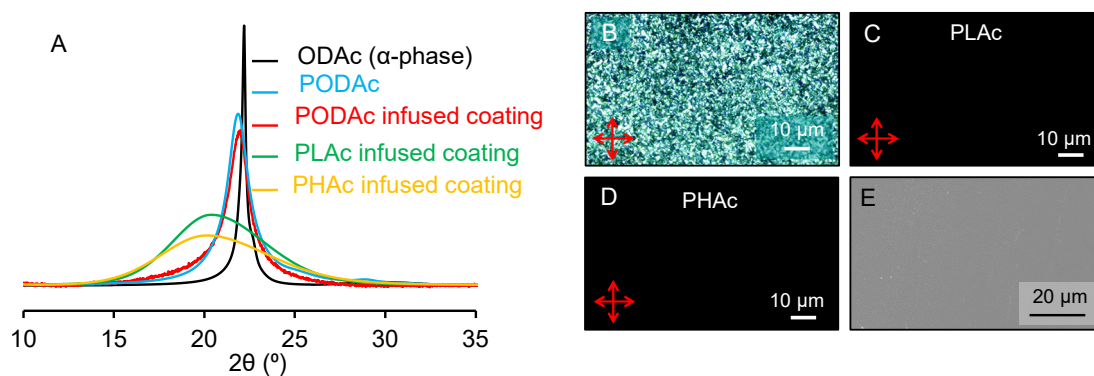


Figure 5.7 A) XRD spectra of ODAc (black), PODAc (Blue) and coatings infused with PODAc (red), PLAc (green), PHAc (yellow). B-D) Cross polar microscope images of PODAc (B), PLAc (C) and PHAc (D) infused coatings. E) FESEM image of PODAc infused coating.

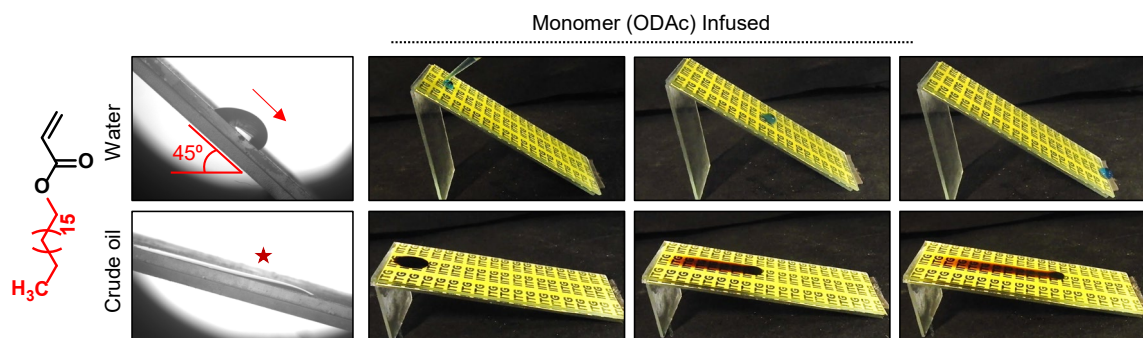


Figure 5.8 Contact angle and digital images depicting the sliding and spillage of water and crude oil droplets on ODAc infused polymeric coating, respectively.

monomer of PODAc in a porous polymeric coating yielded a solid slippery interface below the melting temperature, i.e., 30°C (Figure 5.8). Such an interface remained capable of sliding only the beaded water droplet, however, the beading of crude oil on the same interface resulted in a spillage, as the beaded oil phase readily dissolved the infused monomer, as shown in Figure 5.8. After that, the topography of the PODAc infused solid slippery interface was characterized by field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). On infusion of PODAc, the porous polymeric coating (Figure 5.5A) appeared as a feature-less interface, as revealed by the FESEM images in Figure 5.7E. Furthermore, AFM image analysis revalidated the gradual depletion of the root mean square roughness of the porous polymeric coating from ≈ 407 nm to ≈ 48 nm upon increasing the amount of infused PODAc in porous polymeric coating, as shown in Figure 5.9A. Moreover, magnified AFM images showed the existence of fibril domains (Figure 5.9B) in the polymeric coating— likely because of the crystalline packing of comb-like polymer. Thus, the continuous network of crystalline polymer

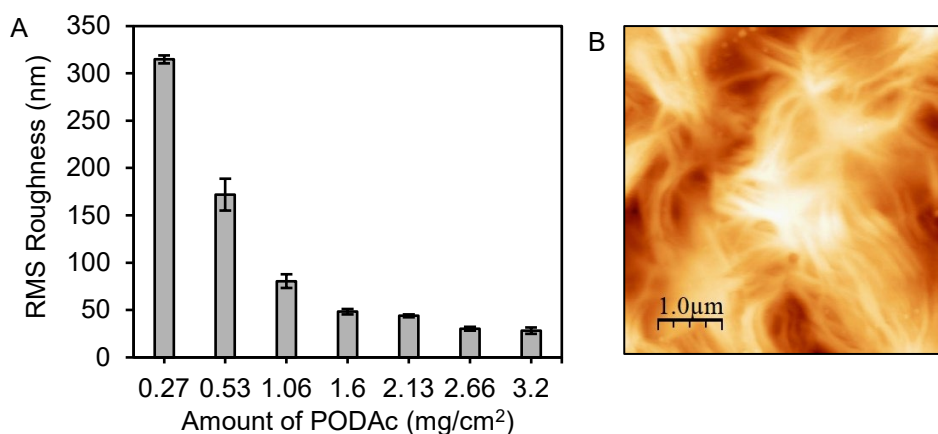


Figure 5.9 A) AFM image of PODAc infused coating. B) Bar diagram showing the changes in root mean square (RMS) roughness (nm) of PODAc infused coatings on increasing its loading amount from 0.27 mg/cm² to 3.2 mg/cm².

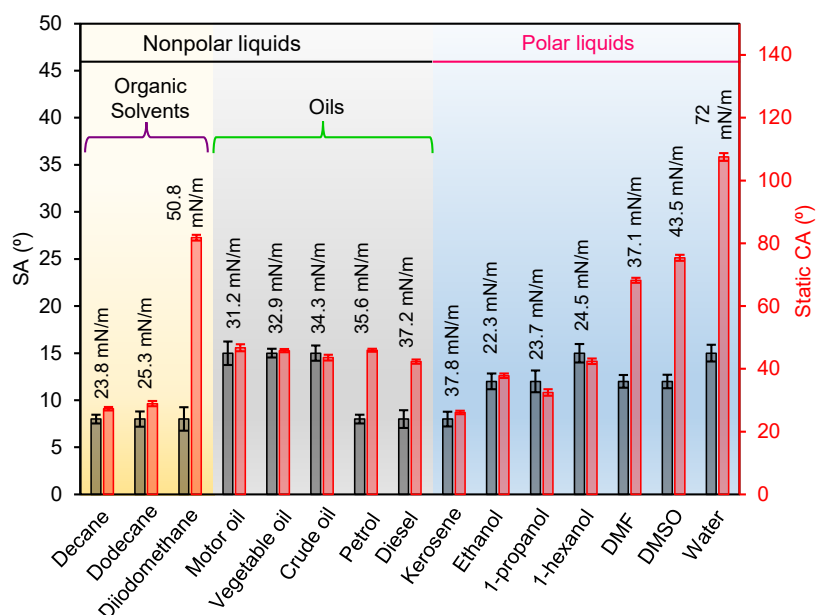


Figure 5.10 Bar diagram of sliding angles (SA) and static contact angles of different non-polar and polar liquids with a wide range of surface tension on PODAc infused coating.

having low roughness (<50 nm) remained instrumental behind the amphiphobic solid-slippy property. In the past, non-fluorinated solid slippy interfaces exhibited efficient sliding of beaded droplets of polar and non-polar organic solvents and water, however, the sliding of relevant and commercially available edible, motor, and engine oils was barely demonstrated. In fact, a nonfluorinated wax-infused slippy coating completely failed to slide beaded droplets of various oils and non-polar solvents (Table 5.1). In contrast, the prepared PODAc infused solid slippy interface was highly efficient at sliding a wide range of beaded droplets of liquids, including water, polar (ethanol, 1-propanol, 1-hexanol, DMSO, DMF), and non-polar (decane, dodecane, diiodomethane) organic solvents and edible (vegetable oil), motor, engine (petrol, diesel, kerosene) oils and crude oil, as shown in Figure 5.10. The static contact

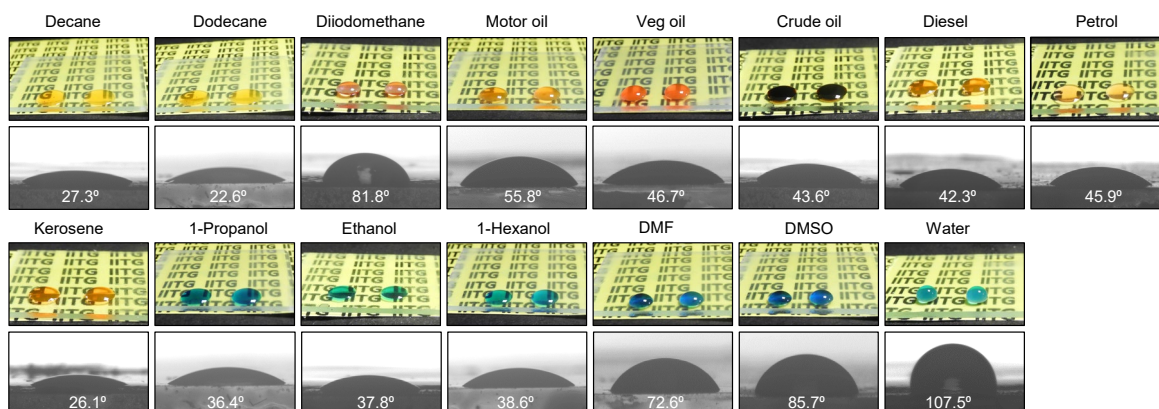


Figure 5.11 Digital images and contact angle images of PODAc infused coating towards different liquid droplets with a wide range of surface tension.

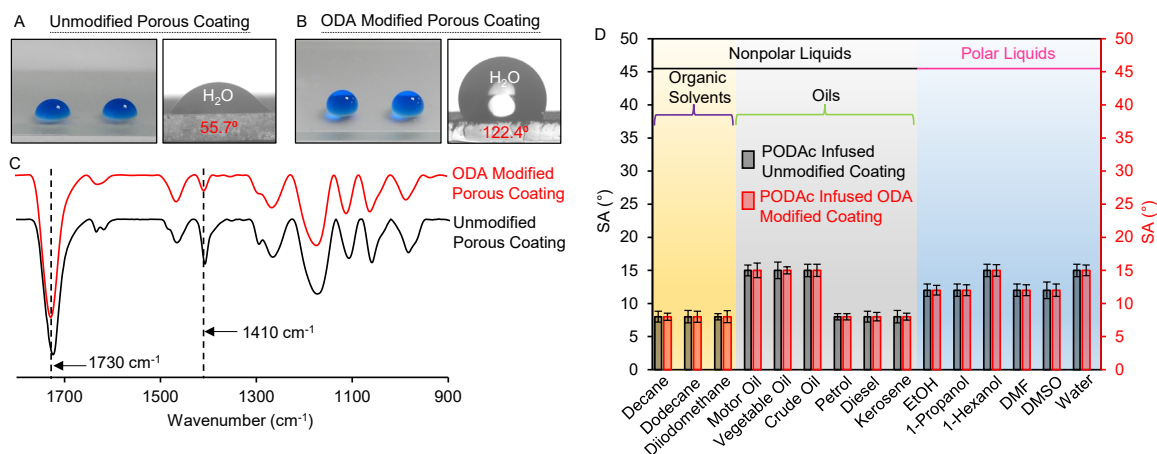


Figure 5.12 A, B) Digital images and contact angle (CA) images of the beaded droplet of water on unmodified (A, hydrophilic) and octadecyl amine (ODA) modified (B, hydrophobic) porous polymeric coating. C) FTIR spectra of unmodified (black) and ODA modified (red) porous polymeric coating. Depletion of the IR peak intensity for C-H deformation of vinyl moiety at 1410 cm⁻¹ with respect to IR signature for carbonyl stretching at 1730 cm⁻¹ confirmed the successful post-chemical modification of porous polymeric coating through 1,4-conjugate addition reaction. D) Bar diagram accounting for the sliding angles (SA) of beaded droplets of different liquids on both the slippery coatings that were derived through the infusion of PODAc (1.6 mg/cm²) in hydrophilic (black, unmodified) and hydrophobic (red, ODA modified) porous polymeric coating.

angles of beaded polar and non-polar liquids on the slippery interface were gradually decreased with lowering the surface tension of the respective liquid, as shown in Figure 5.11. The SAs for the beaded droplets (10 µL) of non-polar organic solvents, petrol, diesel, and kerosene were found to be 8°, whereas the droplets of polar solvents and oils (motor oil, vegetable oil, crude oil) slide off with a little higher tilting angle (≈15°), on the same PODAc infused solid-slippy

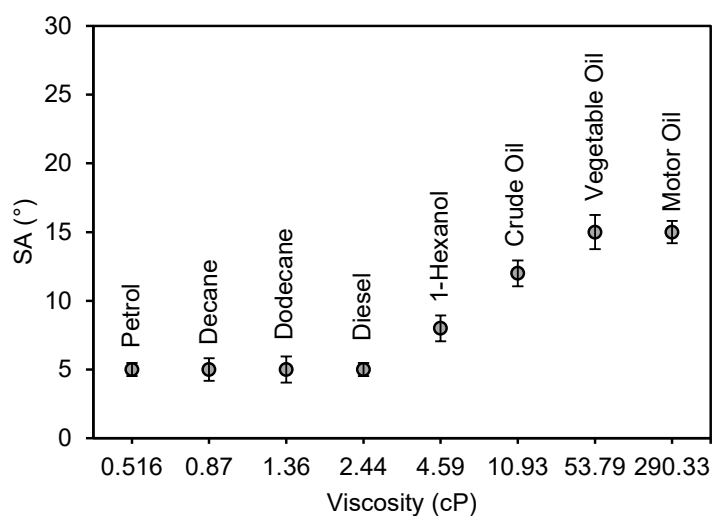


Figure 5.13 Plot illustrating the change of sliding angles of beaded droplets (30 µl) of different polar and non-polar liquids as a function of viscosity.

interface. Interestingly, the change in wettability of the selected porous polymeric coating barely had any impact on the sliding behaviour. In this context, a separate experiment was performed, where the hydrophilic ($\text{WCA} \approx 56^\circ$) porous polymeric coating was postmodified with octadecylamine (ODA) to induce hydrophobicity ($\text{WCA} \approx 122^\circ$, Figure 5.12A–C). However, the separate infusion of the PODAc (1.6 mg/cm^2) in both the hydrophilic and hydrophobic porous polymeric coatings resulted in very similar solid slippery interfaces and any noticeable change in the sliding angle was not observed under an identical experimental set-up (Figure 5.12D). Another important parameter, i.e., viscosity of beaded liquids is known to affect the sliding angle of the solid slippery interface.³¹ In the current study, the sliding angles of beaded droplets of different liquids having a wide range of viscosities were found to be below or around 15° , as shown in Figure 5.13.

5.3.2 Durability of the Developed Solid Slippery Coating

Next, the tolerance of the prepared slippery coating towards various practically relevant outdoor settings was investigated. The synthesized solid amphiphobic slippery property of the PODAc infused polymeric interface remained unperturbed, even after prolonged (15 days) and continuous exposures at extremes of pH (2 and 12), sea water, river water, UV irradiation (254 nm and 365 nm), as shown in Figure 5.14A. The beaded droplets of water, ethanol, petrol, and crude oil spontaneously slide off on the solid slippery interface without any stain and trace of beaded liquid. The prepared slippery coating also survived the prolonged (15 days) exposures

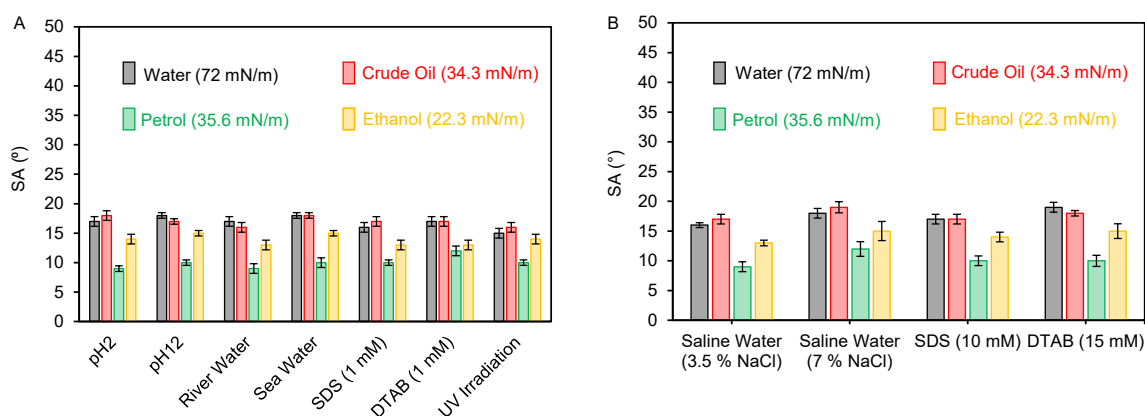


Figure 5.14 A) Bar diagram of sliding angles (SA) of water (black), crude oil (red), petrol (green) and ethanol (yellow) on PODAc infused coating exposed to various harsh chemical environments for 15 days. B) Digital images showing the reversible phase transition of the PODAc polymer upon heating and cooling. B) Bar diagram of sliding angles (SA) of water (black), crude oil (red), petrol (green) and ethanol (yellow) on PODAc infused slippery coating after exposing to high salinity and surfactant contaminated aqueous phase for 15 days.

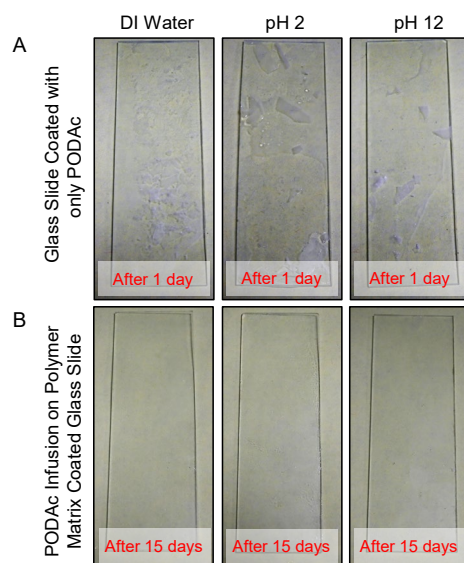


Figure 5.15 A, B) Digital images of bare glass slide coated with only PODAc (A) and porous polymer matrix coated glass slide infused with PODAc (B) after submerging in DI water, pH2 and pH 12 water for 1 day and 15 days, respectively.

to very high salinity (7 wt% of NaCl) and surfactants-contaminated (DTAB, 15 mM and SDS, 10 mM) aqueous phases (see Figure 5.14B). It is worth mentioning that the deposition of PODAc directly on glass failed to sustain even exposure to de-ionized water for 1 day, rather the deposited coating peeled off from the substrate, as shown in Figure 5.15A. The porous polymeric coating played an essential role in achieving a durable amphiphobic solid slippery coating (Figure 5.15B). Further, by taking advantage of the phase transition ability of PODAc, the temperature-assisted self-healing performance of the prepared solid amphiphobic slippery coating was examined. The selected and solid comb-like polymer, PODAc, melted on heating

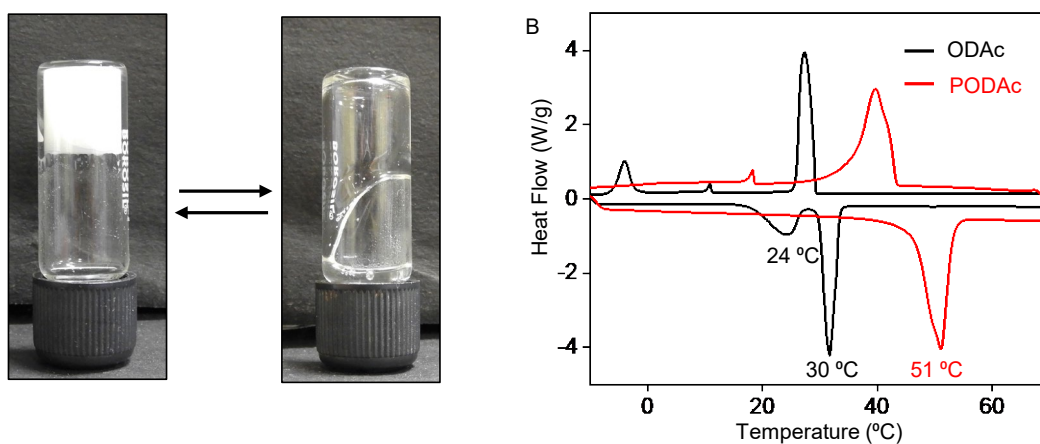


Figure 5.16 A) Digital images showing the reversible phase transition of the PODAc polymer upon heating and cooling. B) Graph showing the phase transition temperature of ODAc (black) and PODAc (red) upon heating.

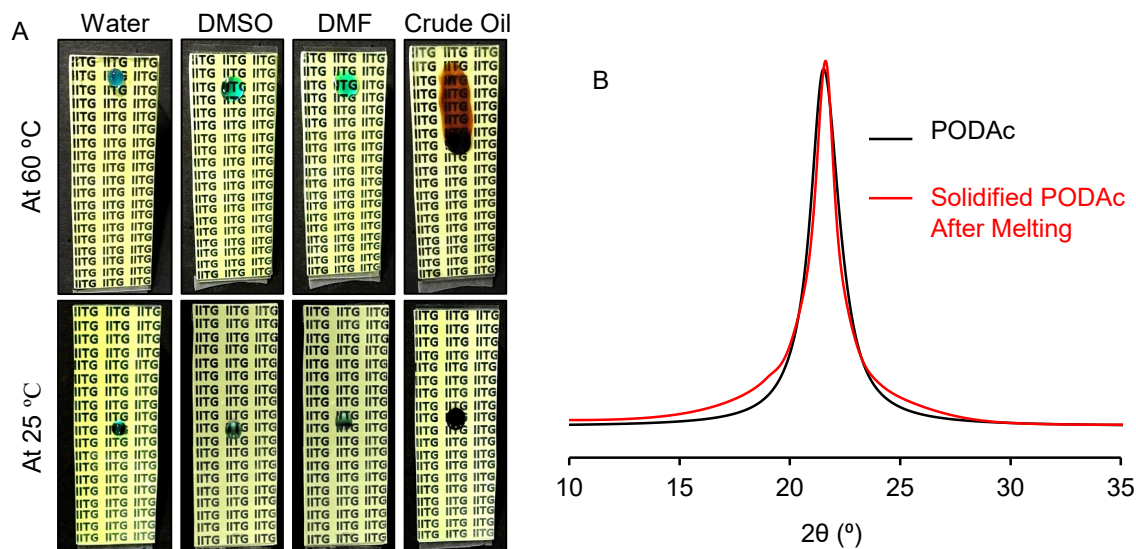


Figure 5.17 A) Digital images showing pinning, spillage and sliding of beaded droplets of water, DMSO, DMF and crude oil on PODAc infused coating after the phase transition above 60 °C and after the solidification of the same interface below the melting point. B) XRD spectra of PODAc infused coating at room temperature before (black) melting and after melting—followed by solidification on cooling (red).

at ≈ 51 °C, and provided a highly viscous liquid. However, the molten and viscous polymer inherently and reversibly solidified on lowering the temperature, as shown in Figure 5.16A. The appearance of an endothermic peak at 51 °C during the differential scanning calorimeter (DSC) analysis precisely revealed the phase transition point, and this phase transition behaviour was found to be significantly different from the respective monomer i.e. ODAc, as shown in Figure 5.16B. As the crystallinity of the infused PODAc is disrupted at the molten state, the phase transition of the infused PODAc temporarily compromised the slippery property. At elevated temperature (60 °C), the beaded droplets of water, DMSO, and DMF on the PODAc-infused polymeric coating failed to slide off, rather they were found to be pinned even at a tilting angle of 90°, and the beaded droplet of crude oil spilled over the coating, as shown in Figure 5.17A. However, the same polymeric interface regained its solid amphiphobic slippery property on cooling it below the melting temperature. As expected, the XRD peak of the PODAc-infused polymeric coating appeared even after solidification of the melted PODAc on cooling (see Figure 5.17B). Thereafter, severe, and multiple physical damage was intentionally incurred on the PODAc-infused solid amphiphobic slippery coating using a sharp knife. The physical damage on the slippery coating was very apparent with the naked eye and optical microscope, as shown in Figure 5.18 A, B. On heating the damaged interface above 51 °C, the reversible and transient fluidity of the molten “comb-like” polymer in the porous polymeric coating helped to heal the physical damage within 50 s, as shown in Fig. 5.18B. As expected,

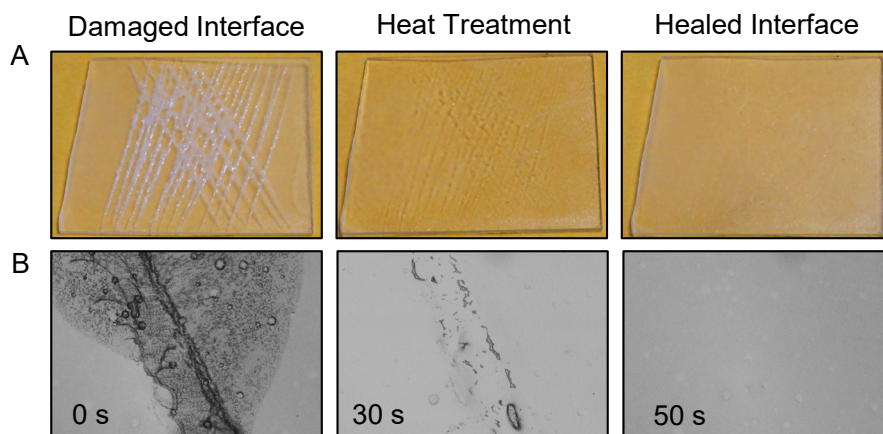


Figure 5.18 A) Digital (A) and microscopic (B) images depicting the thermal-assisted self-healing behavior of physically damaged PODAc infused coating.

the physically damaged interface failed to slide the beaded droplets of water and crude oil, as shown in Figure 5.19A. However, the sliding of beaded droplets of water and crude oil was restored after the temperature-assisted (above 51°C) rapid healing of the damaged interface (Figure 5.19A). These healing and damage cycles were successfully repeated 50 times on the same slippery coating at the same location; however, the sliding behaviour of the beaded droplets of water, polar organic solvent (ethanol), non-polar liquid (petrol), and crude oil remained intact, as shown in Figure 5.19B. Further, such an interface remained highly efficient even after other physical abrasive exposures, including sandpaper abrasion and adhesive tape peeling tests (see Figure 5.20). The report of such non-fluorinated, self-healable, and tolerant amphiphobic solid slippery interfaces that allowed sliding of various polar and non-polar solvents and refined/crude oils is unique and unprecedented.

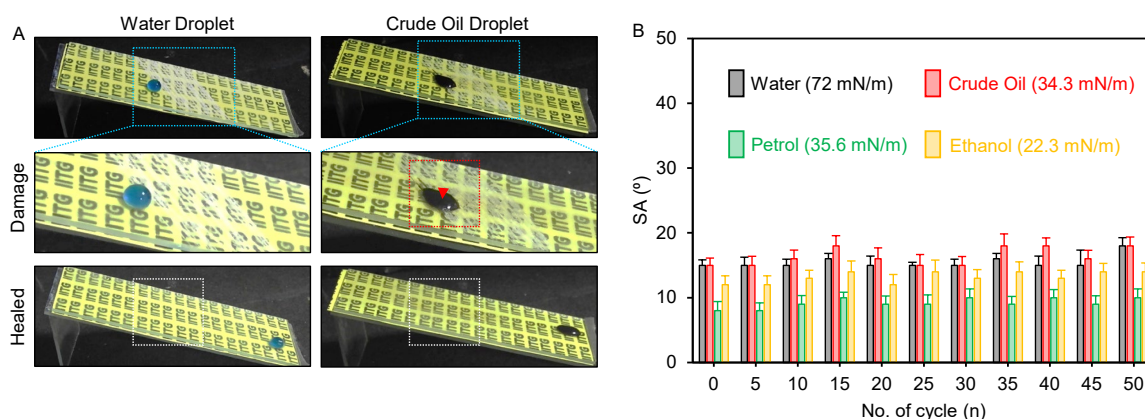


Figure 5.19 A) Digital images illustrating the pinning and sliding of water and crude oil droplet on physically damaged and healed PODAc infused coating. B) Bar diagram showing the impact of repetitive healing and damaging of PODAc infused coating on sliding angles of water (black), crude oil (red), petrol (green) and ethanol (yellow).

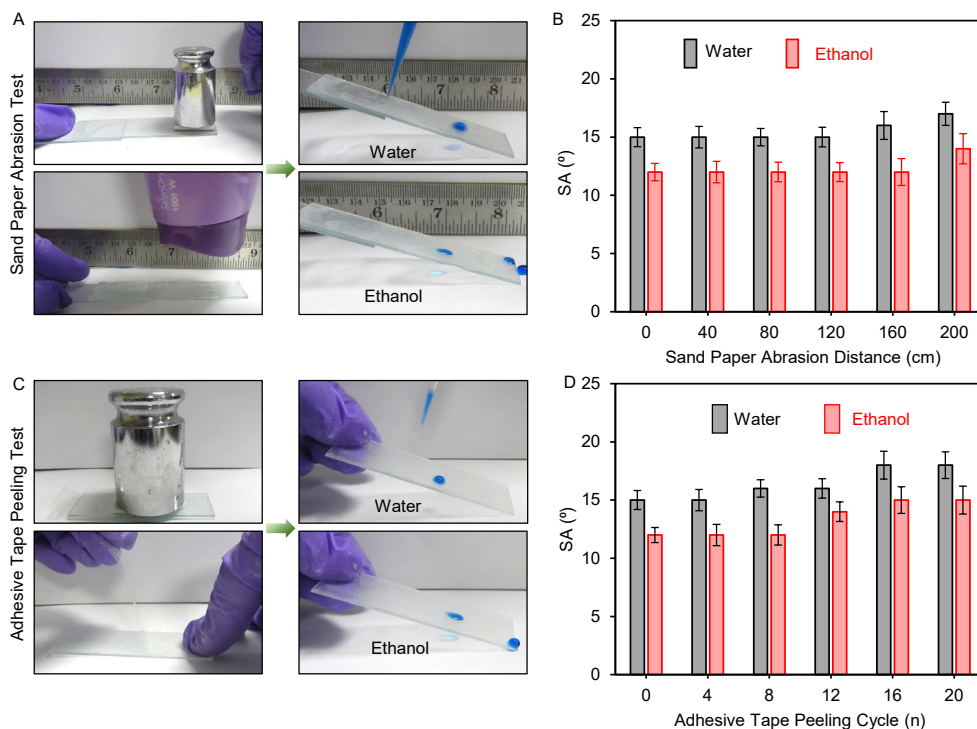


Figure 5.20 A) Digital images showing the sand paper abrasion test on PODAc infused coating and sliding behavior towards water and ethanol. B) Bar graph showing variation of sliding angle of water and ethanol at different sand paper abrasion distance on PODAc infused coating. C) Digital images depicting adhesive tape peeling test on PODAc infused coating and sliding towards water and ethanol. D) Bar graph showing variation of sliding angle of water and ethanol on PODAc infused coating at different adhesive tape peeling cycles.

5.3.3 Substrate Indepency and Scalability

Another important feature of the current design is its substrate-independent and scalable fabrication process. The porous polymeric coating that allowed infusion of PODAc was successfully developed on various substrates, including glass, aluminum foil, printed paper,

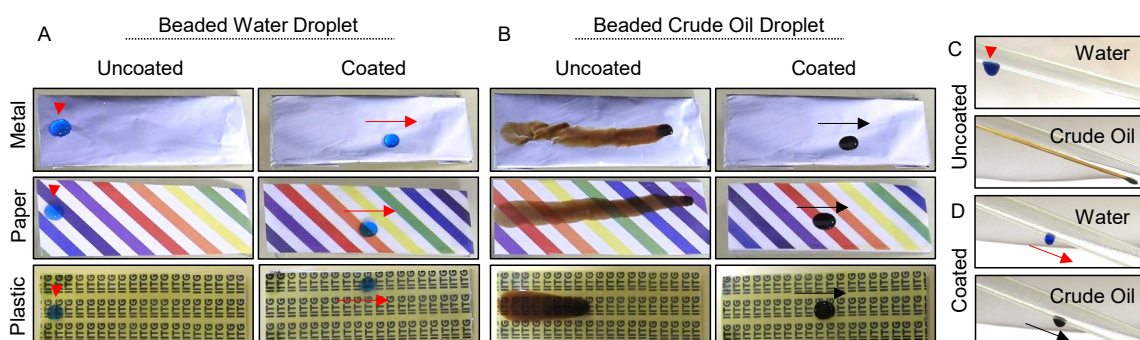


Figure 5.21 A) Photographs illustrating the pinning and sliding of water droplet on uncoated and PODAc infused coated metal, paper, and plastic, respectively. B) Digital images depicting the pinning and sliding of crude oil on different uncoated and PODAc infused surfaces. C, D) Photographs showing the pinning, spreading, and sliding of water and crude oil on both uncoated (C) and PODAc infused coated (D) glass pipe.

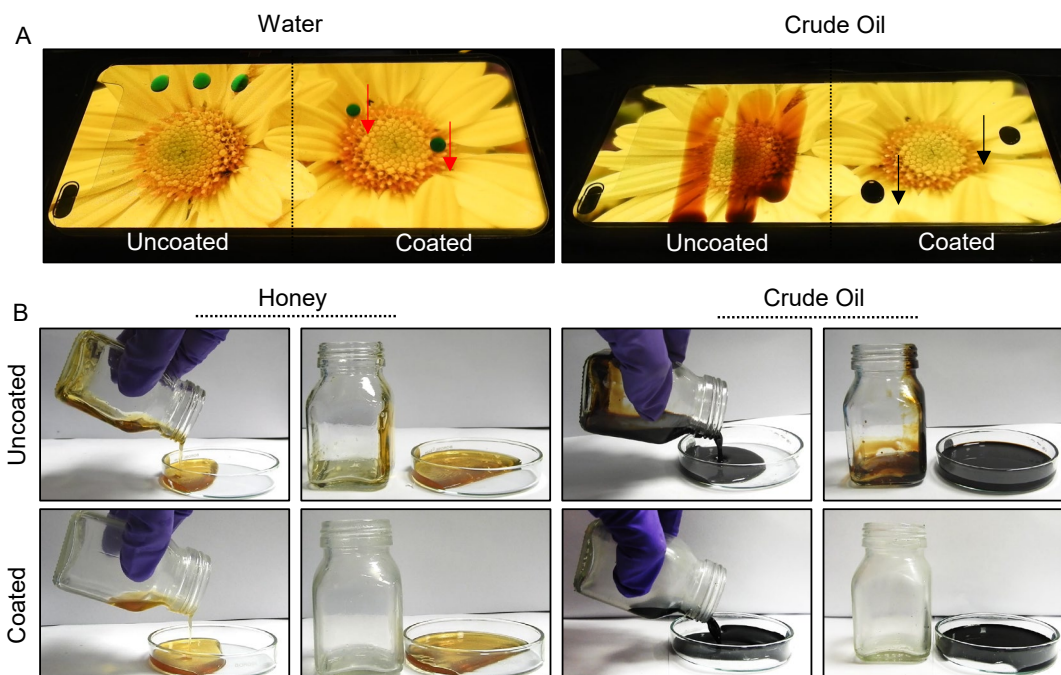


Figure 5.22 A) Digital images showing the pinning and sliding of water and crude oil droplets on uncoated and coated regions of tempered glass of a mobile phone, respectively. B) Demonstrating the dispensing of honey and crude oil from an uncoated and a PODAc infused coated glass bottle.

plastic sheet, etc. to decorate the selected substrates with the amphiphobic slippery properties. As expected, the beaded droplets of water and crude oil were pinned and spilled, respectively, on the uncoated substrates. But, the same substrate decorated with PODAc-infused polymeric coating readily slide off the beaded droplets of both water and crude oil, as shown in Figure 5.21A, B. Further, a curved surface of a glass tube was successfully decorated with the solid slippery property to demonstrate the sliding of both beaded droplets of water and crude oil. But, the uncoated glass tube absolutely failed to do so, instead beaded water and crude oil droplets

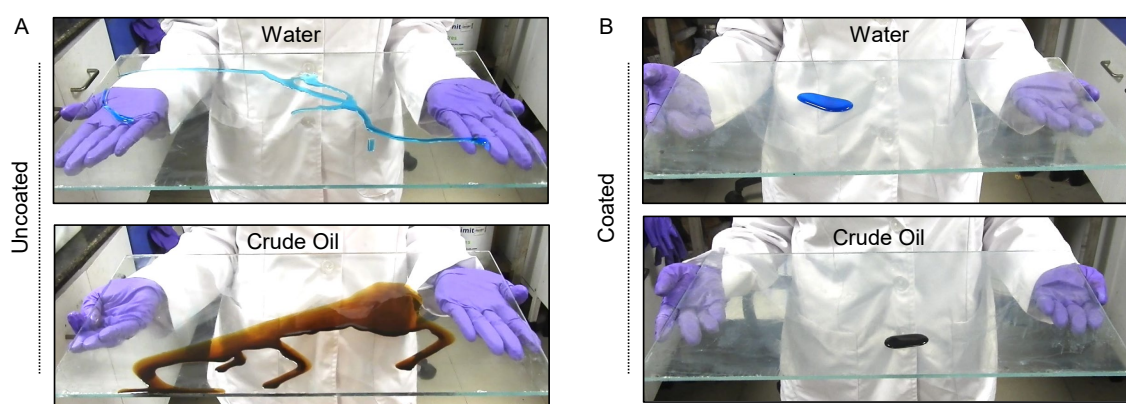


Figure 5.23 A) Illustrating both the spreading (A) and sliding (B) of beaded droplets of water and crude oil on uncoated (A) and PODAc infused coated (1325 cm², B) glass objects, where the coated and uncoated glass substrates were randomly tilted.

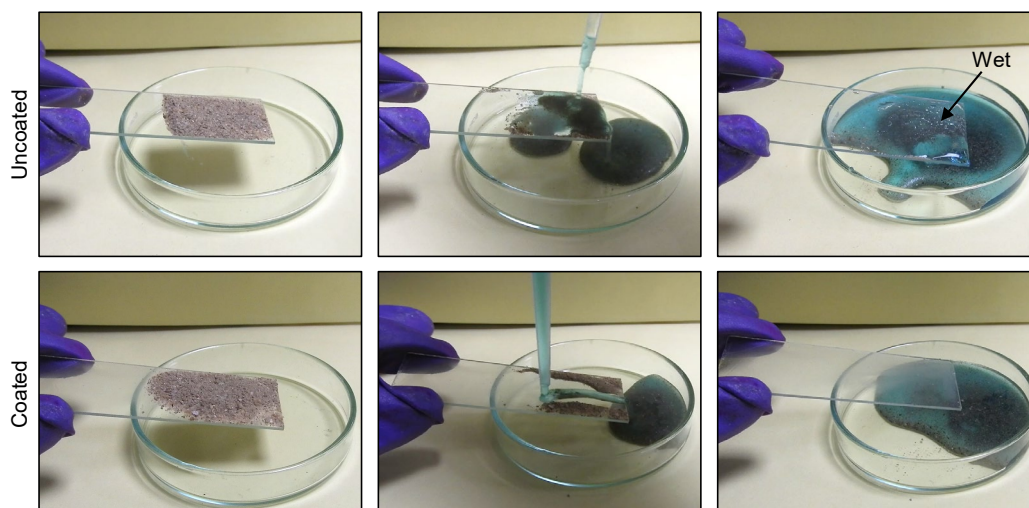


Figure 5.24 Digital images showing the self-cleaning study of sand particles on both uncoated and PODAc infused coated glass slide using water.

were either pinned or spilled, respectively (Figure 5.21C, D). Thereafter, the amphiphobic solid slippery coating was applied on more relevant substrates i.e., safety glass (often called tempered glass) for cell phone display and the interior of a glass bottle. Droplets of water and crude oil readily slide on the coated screen protector of a cell phone, as shown in Figure 5.22A. Honey and crude oil dispense readily and entirely from the coated glass bottle, as shown in Figure 5.22B. The results were also compared with uncoated substrates. The beaded droplets of water and crude oil pinned and spilled all over on uncoated safety glass, and incomplete removal of honey and crude oil from the uncoated bottle remained a common and existing challenge. Thus, the current design of amphiphobic solid slippery interface can be successfully applied on geometrically complex objects (e.g., the interior of a bottle) for realistic and relevant applications. Taking advantage of the simplicity of the fabrication process, the amphiphobic solid slippery coating derived from a comb-like polymer was successfully applied on a large area (1325 cm^2) of a glass substrate. While a droplet (10 mL) of water and crude oil immediately and randomly spilled during random tilting of the bare glass substrate, the beaded droplets of water and crude oil remained well-confined and readily slid on the coated substrate without staining and spilling during random tilting of the substrate, due to the presence of amphiphobic slippery property, as shown in Figure 5.23A, B. Further, such slippery coating displayed self-cleaning ability, as demonstrated in Figure 5.24.

5.4 Conclusions

Thus, the strategic infusion of a “comb-like” polymer comprising long hydrocarbon tails allowed the formation of a crystalline (with hexagonal packing of 4.02° spacing) network in

the porous polymeric coating, to achieve a self-healable, non-fluorinated, and substrate-independent amphiphobic solid-slippy interface. Such a coating remained efficient to successfully exhibit sliding of various liquids, including water, polar and non-polar solvents, different commercially available refined oils, and crude oil. The solid slippy coating presented in this work is capable of repetitive (at least 50 times) and rapid (less than 1 minute) self-healing of physical damage, thus allowing the material to regain its embedded slippy property. Moreover, the intact slippy property of the coating even after prolonged (15 days) exposures to various complex aqueous phases and UV-irradiation justified its appropriateness for performing at various and severe outdoor settings. Thus, the adapted chemical approach presented can be exploited for multiple future applications through the strategic design of different functional “comb-like” co-polymers.

5.5 References

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Chapter 6: Conclusions and Future Directions

This chapter gives an overview of the previously discussed chapters. This thesis outlines the strategic utilization of a facile and catalyst-free 1, 4-conjugate addition reaction between amine and acrylate functional groups for developing liquid-repellent surfaces with enhanced robustness and durability following a simple, scalable, and rapid fabrication approach. In Chapter 1, I have provided a concise overview of bio-inspired wettability, general methods adopted to develop artificial anti-wetting surfaces, existing challenges, and objectives behind this thesis work. Chapter 2 demonstrates the strategic use of a catalyst-free 1,4-conjugate addition reaction between distinct and strategically selected small molecules allowed to prepare an active deposition solution with prolonged shelf-life in various and commonly used reaction media to derive optically transparent superhydrophobic coating. In Chapter 3, I have introduced a covalent cross-linking chemistry between selected reactants to achieve tolerant and hard superhydrophobicity. In Chapter 4, I have demonstrated the design of chemically functionalizable coatings with a combination of a physically unclonable porous topography and distinct physiochemical properties (e.g., fluorescence, water wettability, and water adhesion) obtained through orthogonal chemical modifications (i.e., 1,4-conjugate addition reaction and Schiff-base reaction at ambient conditions) for multilevel anti-counterfeiting application. Chapter 5 accounts for the utilization of a crystalline comb-like polymer to derive a non-fluorinated, substrate-independent, and self-healable amphiphobic solid slippery coating following a simple and scalable fabrication process.

In recent years, superhydrophobic surfaces have gained significant interest in application in various research topics, such as wearable sensors, catalytic electrodes, photothermal manipulation, etc. Underwater vibration sensing has substantial importance in human safety, military defence, environmental protection, disaster prevention, etc. The performance of such devices mainly depends on the metastable trapped air and hydrophobicity. Most of the presented sensing devices lose their efficiency due to hydrophilicity. Hence, the amalgamation of hydrophobicity with these sensing devices will be an important avenue to ensure the working stability and lifetime of the device. Another notable challenge faced by these devices is material flexibility and substrate attachment. In this context, hard and tolerant superhydrophobic materials presented in this synopsis report with the integration of conductivity can be explored in developing underwater vibration sensing devices. Strategic association of conductive materials such as graphene, silver nanowires, carbon nanotubes, polypyrrole, etc, in the reaction mixture described in Chapter 3 would allow the development

of conductive and robust superhydrophobic coated substrates in a single step. The mechanical properties and wettabilities of selected substrates can be tuned through the strategic choice of appropriate crosslinkers and hydrophobic molecules. The effect of tailoring mechanical properties and wettabilities on the performance of the sensing device will be an important aspect to explore in future.

Although superhydrophobic surfaces have enormous prospects for various relevant applications, but mostly reported surfaces are chemically inert in nature. Hence, it is always challenging to customize superhydrophobicity and chemical reactivity on the same surface. In the past, chemically reactive surfaces have been used to create patterns with heterogeneous wettability, and they have a wide range of applications in energy harvesting, microfluidics, biomedical detection, water harvesting, etc. Hence, the chemically functionalizable porous polymeric coating outlined in this synopsis report consists of orthogonal reactive residual amine and acrylate groups and can be used further for selective modification with hydrophilic and hydrophobic molecules for different wettability patterning to showcase relevant practical applications such as in microfluidics, cell culture, microdroplet arrays, etc.

Further, the developed amphiphobic solid slippery coated surfaces discussed in this synopsis report can be used to derive smart windows capable of fine-tuning the solar spectrum exposure and controlling the energy requirement to maintain the temperature of a building. Also, functionalization of slippery surfaces with micro/nano patterns will broaden the scope for applications such as water harvesting, microdroplet arrays, directional transport of liquid, etc. It is challenging to create amphiphilic-amphiphobic patterned interfaces. As a result, designing a chemically reactive amphiphobic solid slippery surface can provide a solution to derive a patterned slippery interface combining amphiphobic and amphiphilic wettabilities through a post-functionalization approach. Therefore, these developed liquid repellent materials exhibit significant versatility and can be used in various further relevant research topic.

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12. D. Parbat, N. Jana, **M. Dhar**, and U. Manna, *ACS Appl. Mater. Interfaces*, 2023, **15**, 25232—25247.

Patents

1. U. Manna, **M. Dhar**, Preparation of substrate independent, healable and amphiphobic slippery coating. Indian Patent, Application No.: 202131056900, Date: December 07, 2021.
2. U. Manna, A. Das, **M. Dhar**, "A sorbent material for distillation-free separation and recovery of floating oil contaminants", Indian Patent, Application No. 202131020005, Filling Date: April 30, 2021.
3. U. Manna, V. P. Nandakumar, K. Ramalingam, M. M. G. BHAT, P. K. HEGDE, A. Das, A. Shome, **M. Dhar** "A coating composition and a process of preparation thereof" Indian Patent, application 202041020725, Filling Date: 16.05.2020

Conferences Attended

1. Poster presentation at **17th International Conference on Polymer Science and Technology (SPSI-MACRO-2023)** from 10th to 13th December, 2023 organized by IIT Guwahati.
2. Poster presentation at **Seventh International Conference on Multifunctional, Hybrid and Nanomaterials**, Geona, Italy from 19th to 22nd October, 2022.
3. Poster presentation at **ACS Fall 2022 Sustainability in a Changing World, Hybrid** – Chicago, IL and virtual from 21st to 25th August 2022. (Selected for Sci-Mix)
4. Oral pitch at **ACS Fall 2022-India Satellite Event** (August 2022).
5. Poster presentation at **CRSI-NSC-28: 28th National Symposium in Chemistry** from 24th to 27th March 2022 organized by IIT Guwahati, India.
6. Poster presentation at **International Conference on Advanced Materials and Mechanical Characterization** from 2nd to 4th December 2021 organized by SRM University, India.

Awards and Achievements

1. **Best research pitch award** at ACS Fall 2022-India Satellite Event (August 2022).
2. **Second prize** in the 7th International Conference of Bionic Engineering & the International Youth Conference of Bionic Science and Engineering 2022 (ICBE & IYCBSE 2022), Wuhan, China.
3. **Best poster award** at 28th CRSI National Symposium in Chemistry, India (February 2022).
4. **Best poster award** at the International Conference on Advanced Materials and Mechanical Characterization (ICAMMC-2021), India (December 2021).