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Sprayable Superhydrophobic Coating with High Processibility and Rapid Damage-Healing Nature

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Abstract

Superhydrophobic coatings simultaneously exhibiting high substrate binding, mechanical robustness and damage-healing properties are of great significance for practical applications. In this work, an effective silicone-based paint was developed to prepare superhydrophobic coating for the first time with the abovementioned properties. The paint is formulated with supramolecular silicone polymers and silica nanoparticles, which can be sprayed on solid substrates and assembled into porous films with enhanced water repellency. The abundant hydrogen bonds and coordination bonds in the supramolecular silicone polymers provided additional substrate binding and damage-healing properties. The coating can maintain water-repellency upon a series of tests including tape peeling, sandpaper abrasion and underwater placement. They can repeatedly heal chemical and topographical defects by simple thermal treatment due to the dynamic intermolecular crosslinking and chemical reorganization of the supramolecular polymers. Taking advantages of their high processibility, multifaceted robustness and inherent healing ability, the developed superhydrophobic coatings hold great promise for applications in liquid transportation, oil-water separation, anti-icing and drag reduction.

Keyword: Superhydrophobic, mechanical robustness, damage-healing property, high processibility, liquid transportation

1. Introduction

Superhydrophobic coatings are widely used in daily life and industry[1, 2], because they can provide robust liquid-repellency and enable self-cleaning[3, 4], anti-icing[5, 6], corrosion-resistance[7-9], oil-water separation[10-12], and water manipulation[13, 14]. Various fabrication technologies have been developed to prepare superhydrophobic coatings with desired features and functions to meet specific requirements in various applications[15-19]. However, most superhydrophobic coatings still suffer from the lack of mechanical robustness and the loss of liquid-repellency upon mechanical damages[20]. For example, the microstructures of the coating can be easily destroyed by different types of mechano-chemical damages, such as tape-peeling, knife-scratch, sandpaper abrasion, and plasma treatment[21]. These drawbacks have seriously hindered their practical applications.

Recently, several strategies have been reported to improve the durability of superhydrophobic coatings by using materials with high mechanical strength and robustness, such as, polymer nanocomposite[22, 23], ceramics[24, 25], metals and metal alloys[26, 27]. Although such strategy can reinforce the durability of superhydrophobic coatings against various destructions in harsh environment, it cannot avoid the generation and accumulation of micro-scaled defects during the usage, which will eventually lead to the loss of the liquid repellency. In this regard, endow superhydrophobic surface with reliable damage-healing properties to help recover from both chemical and mechanical defects, has been demonstrated as a promising approach. For example, the migration of pre-stored hydrophobic molecules to the air-solid interface can help restore the chemical defect of the superhydrophobic surface after plasma treatment[28-32]. However, this strategy can rarely help repair physical or mechanical damages. Alternatively, shape memory polymers[33], have been reported to recover structure collapse, but they are not tolerant to other types of mechanical damage, such as scratches or abrasions. Therefore, to develop durable superhydrophobic coatings with reliable damage-healing properties, the effect of the material

chemistry and composition on the recovery of surface and structural integrity should be duly considered.

Supramolecular chemistry has been extensively used for construction of various functional polymers, especially healable materials. Among them, silicone-based polymers with healable function have attracted tremendous attention due to their potential applications in flexible electronics, wearable devices and soft robotics[34-37]. There are a few examples of using supramolecular silicone for coating development, such as the damage-healable slippery or oil-repellent surface[38-41]. Recently, silicone based supramolecular nanocomposites with damage-healing and superhydrophobicity are also reported[42]. However, these supramolecular nanocomposites are processed and evaluated as bulk materials such as foam and aerogel. Their processibility, substrate binding, damage healing as a coating on solid substrates are elusive.

Herein, we developed a superhydrophobic coating with a combination of features that have been rarely achieved simultaneously including high substrate binding, mechanically robustness, reliable and rapid damage-healing on both chemical and mechanical defects. We firstly synthesized a supramolecular silicone polymer with high mechanical stability and damage-healable property[43]. Then, an easy operational superhydrophobic paint was achieved by simply dispersing supramolecular silicone polymer and silica nanoparticles in THF for further water-repellent treatment of various substrates. After spraying onto the substrate, it assembled into porous film and displayed typical superhydrophobicity with a high water contact angle of $157.2 \pm 1.9^\circ$ and a low water sliding angle of $7.8 \pm 0.8^\circ$. Due to large amount of hydrogen-bonds and coordination bonds between the film and substrates, the coatings exhibited excellent mechanical robustness against repeated tape peeling tests, sandpaper abrasion and long-time of underwater placement. More importantly, topographical defects and surface chemistry can be recovered by simple thermal treatment due to the dynamic intermolecular crosslinking and chemical reorganization of the supramolecular polymers. Along with high processibility, multifaceted

robustness and inherent healing ability, the developed superhydrophobic coatings offer tremendous possibilities for numerous applications, such as liquid transportation, oil-water separation, anti-icing and drag reduction.

2. Experimental Section

Materials: Bis-aminopropyl-terminated polydimethylsiloxane (PDMS, $M_w=870$) was purchased from Gelest, Inc. Dopamine hydrochloride (DOPA), isophoronediiisocyanate (IPDI) and other chemicals/solvents were purchased from Sigma-Aldrich. Silica nanoparticles were purchased from Shan Yi Plastic Co. LTD. Various substrates, including glass slide, stainless steel mesh, silicon wafer, aluminium sheet, cotton fabric, paper and filter paper, melamine sponge, were commercially available. All chemicals were used as received. The substrates materials were treated by ultrasonic washing in ethanol before use.

Synthesis of superhydrophobic paint: Firstly, the supramolecular polymer (PDMS-Cat-Zn) was prepared according to our previously published method[43]. Briefly, 5 mmol PDMS, 5 mmol DOPA and 0.5 mmol IPDI were blended to synthesis PDMS-Cat, followed by coordination with Zn (II) ion (2.5 mmol) to obtain PDMS-Cat-Zn supramolecular silicone polymer. Then, superhydrophobic paint was prepared by mixing silica nanoparticles and supramolecular silicone polymer with various weight ratio from 0 to 40 wt% in THF (10 mL) to form a homogenous solution. After 0.5 h stirring, the paint was ready for applying on various substrates.

Fabrication of superhydrophobic surface: Superhydrophobic nanocomposite coating can be obtained by simply spraying supramolecular silicone polymer/silica nanoparticles suspension onto the substrates. Besides, by adjusting the spraying volume (0.3, 0.6, 0.9 mL), nanocomposite films with different thickness (30, 60, 90 μm) could be obtained.

Shear strength test: Superhydrophobic paint with various silica nanoparticle concentration (0, 10, 20, 30, 40 wt%) was firstly deposited onto a glass slides, followed by pressing another glass

above it to ensure uniform and firm contact after curing. Shear strength tests were performed on Instron 5566 and the strain rate was 10 mm/min, and the shear strength was acquired by testing break stress.

Tape-peeling test: A standard Elcometer 99 tape (adhesion to steel: 642 N/m) was used to assess coating degradation. After applying 1 kg weight, tape was peeled off from the substrate. The water contact angle, water sliding angle of the composite coating were measured after every 20 cycles of abrasion.

Abrasion test: A 1 kg weight was placed on the sandpaper (grit no. 220, 2.5 cm x 2.5 cm) and sample was underneath. Then the sandpaper was pulled in one direction at a constant speed of 0.2 cm/s (Figure 4a down). The water contact angle, water sliding angle and the weight of the composite coating were measured after every 10 cycles of abrasion.

Mechanical damage-healing process: Notch penetrating to the underlying substrate was made on the nanocomposite coating with different thickness (60, 90, 120 μm) by using a razor blade. After that, the surface was heated at different temperature for different times to investigate their healing property.

General characterizations: The wetting properties of static and dynamic contact angles of the coatings were measured with a customized system. The volumes of droplets used for static contact angle and sliding angle measurements were 6 μL and 10 μL , respectively. The micro-nano structures and thickness of the composite coatings on the glass slide was investigated by using a field emission scanning electron microscope (SEM, Philips XL30CP) at 10.0 kV. An energy dispersive X-ray spectrometer (EDS, Oxford Instruments INCA Energy 200) was used for elemental analysis. Fourier transform infrared (FTIR) spectroscopy was performed with a Perkin Elmer Spectrum 100 instrument. The surface chemical composition was performed by using a Kratos Axis-Ultra HAS X-ray photoelectron spectrometer (XPS). The thermogravimetric analysis (TGA) was examined on a TA Q600 differential thermal analyzer at a heating rate of $10^\circ\text{C min}^{-1}$.

The differential scanning calorimetric (DSC) curves were recorded on a TA DSC25 machine with a temperature cycle $-80^{\circ}\text{C} \sim 80^{\circ}\text{C}$. The rheological measurements were performed on a rotational rheometer (Malvern Kinexus Lab+). The damaged and healed process of the paint was observed by an upright optical microscope (Nikon Eclipse Ni-U). The other optical images and videos were taken by a SLR camera (Nikon D5500). The microindentation test was performed on a Fischer HM2000XY Micro-Hardness Tester in a displacement-controlled mode and the load force was controlled 100 mN.

3. Results and discussion

The chemical structure of supramolecular silicone polymer was shown in Figure 1a. This supramolecular polymer contained flexible PDMS backbones and crosslinked by dynamic hydrogen bonds and coordination bonds (Figure 1b), which enabled desirable mechanical strength, high substrate binding and thermally healable property. The superhydrophobic paint was prepared by simply mixing supramolecular silicone polymer and silica nanoparticles in THF solvent, which could be applied on various substrates via simple spraying method (Figure S1). After modification, various substrates all showed remarkable superhydrophobicity (Figure S2) and the water droplet can bound on the coating surface (Figure 1d), demonstrating its excellent superhydrophobic performance.

The chemical composition of the composite coating was confirmed by Fourier transform infrared (FTIR) spectroscopy, and energy dispersive X-ray spectrometer (EDS). As displayed in Figure S3a, superhydrophobic coating exhibited many strong absorption peaks corresponding to the stretching vibrations of PDMS ($700\text{-}1300\text{ cm}^{-1}$), uredo units ($1500\text{-}1700\text{ cm}^{-1}$) and hydroxyl functional groups ($3300\text{-}3400\text{ cm}^{-1}$), which were all from supramolecular silicone polymer. There was no distinct signal of silica nanoparticles in the composite coating because silica nanoparticles were fully encapsulated by the polymer. Besides, EDS spectra also confirmed that the elements

of C, N, O, Si, Zn were uniformly distributed on the surface of superhydrophobic composite coating, demonstrating that the coating successfully covered on the glass (Figure S3b, c).

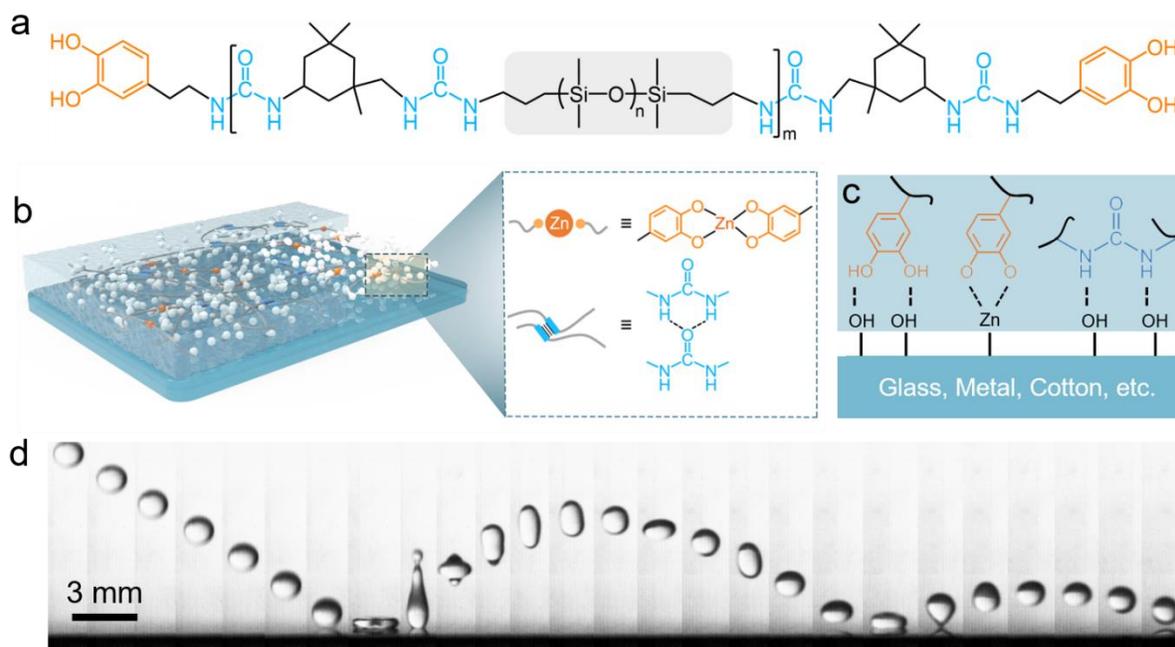


Figure 1. Design of the healable superhydrophobic coatings. a) Chemical structure of supramolecular silicone polymer. b) Schematic structure of the superhydrophobic nanocomposites. Double dynamic bond containing both reversible hydrogen bond and metal-ligand constructed hybrid dynamic networks. c) Schematic diagrams of high binding ability of the superhydrophobic coating with various substrates via different chemical interactions. d) The water droplet bouncing process on a horizontally placed spray-coated glass. Time intervals are ~ 12 ms.

The native supramolecular silicone polymer is moderate hydrophobic, with a water contact angle of $91.0 \pm 1.8^\circ$ when it is cast on glass slide to form a flat film (Figure S4). To further enhance the water repellency, hydrophobic silica nanoparticles were blended with the polymer to improve surface roughness[44, 45]. As shown in Figure 2a, b and Figure S5, at lower loading amount of silica nanoparticles (10, 20 wt%), the coating surface shows smooth morphology with a water contact angle below 150° . When the loading amount increased to 30 and 40 wt%, hierarchical roughness was formed, for which large quantities of polymer-warped particles were observed at

the coating surface (Figure 2c, d). Those coatings exhibited typical superhydrophobicity. For example, coatings with 30 wt% silica nanoparticles exhibited a high water contact angle of $157.2\pm 1.9^\circ$ and a low water sliding angle of $7.8\pm 0.8^\circ$ (Figure 2e).

According to our results, nanocomposites with 30, 40 wt% silica nanoparticles exhibited best water-repellency. Then, the influence of silica nanoparticles on the mechanical strength and healing ability was systematically studied. Results of micro-indentation and shear strength tests showed that the mechanical strength has been enhanced with increasing silica nanoparticles from 0 wt% to 30 wt% because inherent hard property of silica nanoparticles brought larger mechanical strength (Figure 2f, g). However, when further increasing to 40 wt%, binding force between silicone polymer and silica nanoparticles or substrates decreased, which weakened the interfacial binding force. Therefore, nanocomposites with 30 wt% silica nanoparticles were selected for the following researches.

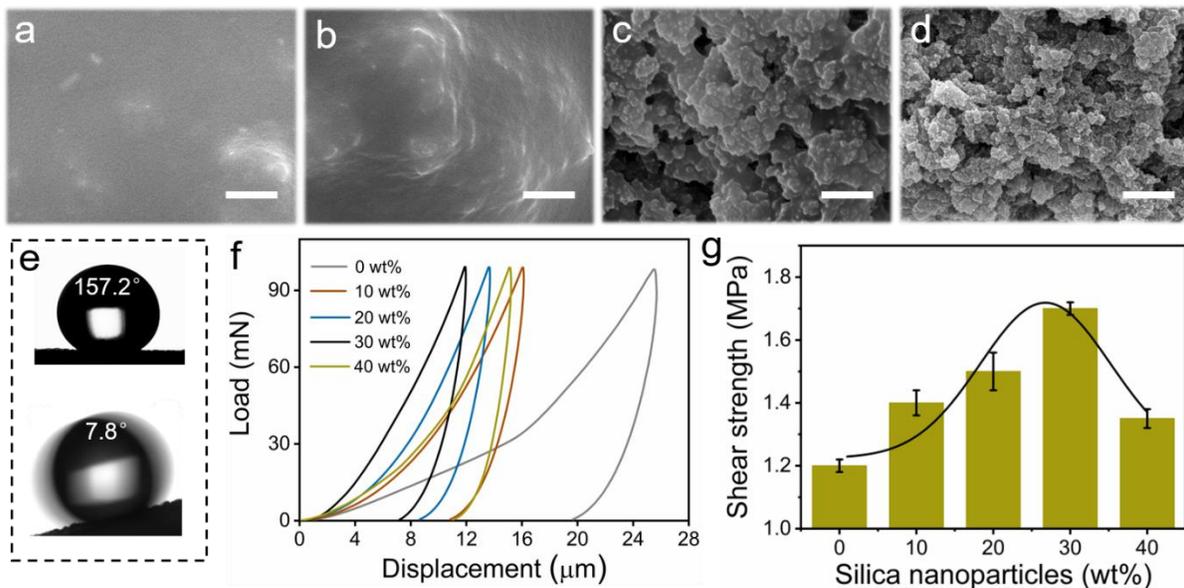


Figure 2. Morphology and mechanical properties of the composite coatings. a-d) SEM images of nanocomposites when loading different concentration of silica nanoparticle (10, 20, 30, 40 wt%). e) Water contact angle and water sliding angle of the nanocomposite coating when loading 30

wt% silica nanoparticle. f, g) Micro-indentation and shear strength of the nanocomposite coatings with different concentration of silica nanoparticles. Scale bar is 2 μm .

Recently, there are a few reports on supramolecular superhydrophobic composites with damage-healing ability[42, 46], but they are mostly confined to bulk materials, and the rationale on the damage-healing mechanism as a coating has not been well addressed. In a typical damage-healing test shown in Figure 3a, a scratch with about 10 μm width on the sample film with 60 μm thickness coated on glass slide could be fully healed in 3 minutes under heating at 120°C, which was contributed to the dynamic non-covalent bonds in the supramolecular silicone polymer (Figure 3b). Actually, the glass transition temperature of the pristine silicone polymer was slightly above room temperature, at 40.9°C (Figure S6). Temperature around 60°C is needed to proceed the phase-transition and thus the damage-healing process of the polymer[43]. After incorporation of silica nanoparticles, the rheological properties of the silicone polymer after phase transition have been altered because silica nanoparticles will increase viscosity, retarding migration of polymer chain to heal physical damage (Figure 3c). Indeed, self-healing ability could be achieved only when loadings of silica nanoparticles below 40 wt% (Figure S7). Thus, a higher temperature (around 80°C) was required to decrease viscosity of the nanocomposite coating, enabling the composite coating with high mobility and simultaneously convert the equilibrium of dynamic non-covalent bonds to a disassociated state. Therefore, after heating above 80°C, the silicone polymer nearby the damage region tended to move to the void area to reconnect and reform hydrogen bonds and catechol-Zn coordination bonds, then healing microscopic defects. As it shown in Figure 3d and Figure S8, this healing process could be more rapidly completed under smaller damage depth. High temperature could accelerated the healing speed due to higher mobility of supramolecular silicone polymer at elevated temperature. The reliability of such damage-healing process was continuously tested and after 10 damage-healing cycles, the superhydrophobicity of the film was well maintained (Figure 3e). Except for physical defects, surface chemistry can also be recovered, which was discussed in supplementary information (Figure S9).

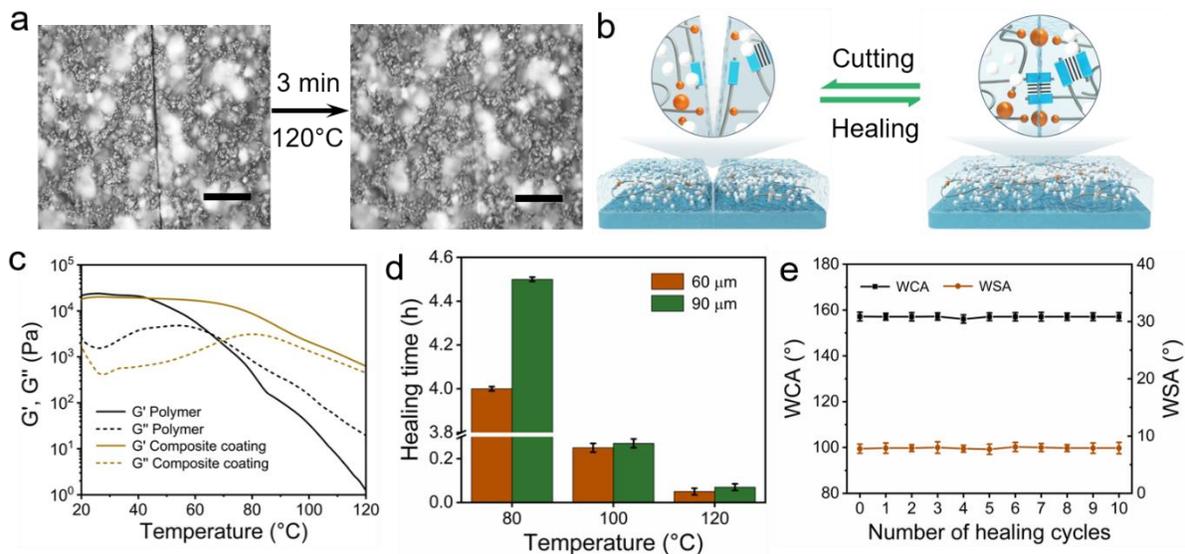


Figure 3. Mechanical damage-healing test on the superhydrophobic nanocomposite films. a) Microscopic images of the nanocomposite coating damaged by knife-cutting (left) and after healing (right). b) Schematic diagram of damage-healing process. c) Rheological properties of silicone polymer and nanocomposite coating. d) Healing time of nanocomposites under different damage depth and heating temperature. e) Continuous evaluation of the water-repellency under repeated damage-healing cycles. Scale bar is 100 μm .

In order to evaluate its feasibility in practical applications, mechanical robustness should also be taken into consideration. Firstly, inner adhesion between the silica nanoparticles and silicone polymer was evaluated by tape-peeling test (Figure 4a up). As displayed in Figure 4b-c, the composite coating maintained superhydrophobicity and porous structure even after 40 times of tape peeling, indicating strong interfacial binding between silica nanoparticles and silicone polymer. We also performed a cross-hatch, a more standard adhesion test to further confirm the robustness (Figure S10).

Besides tape-peeling test, sandpaper abrasion was also carried out to verify the mechanical durability (Figure 4a down). As shown in Figure 4d, the surface still remained superhydrophobicity with a high contact angle above 150° and a low sliding angle below 10° even

after 80 cycles of abrasion. 100 cycles of abrasion would slightly crush the hierarchical structure and weaken water-repellency with water contact angle and water sliding angle of 151.6° and 33.2°. However, after heating at 100°C, the mobility of the supramolecular silicone polymer was activated and restored hierarchical structure due to phase transition of silica nanoparticles and silicone polymer (Figure 4e-f), restoring superhydrophobicity. Moreover, the coating was also very stable underwater (Figure S11a-b). After 24 h of underwater placement, air-cushion still formed on the surface (Figure S11c) and water still could slide off the surface easily.

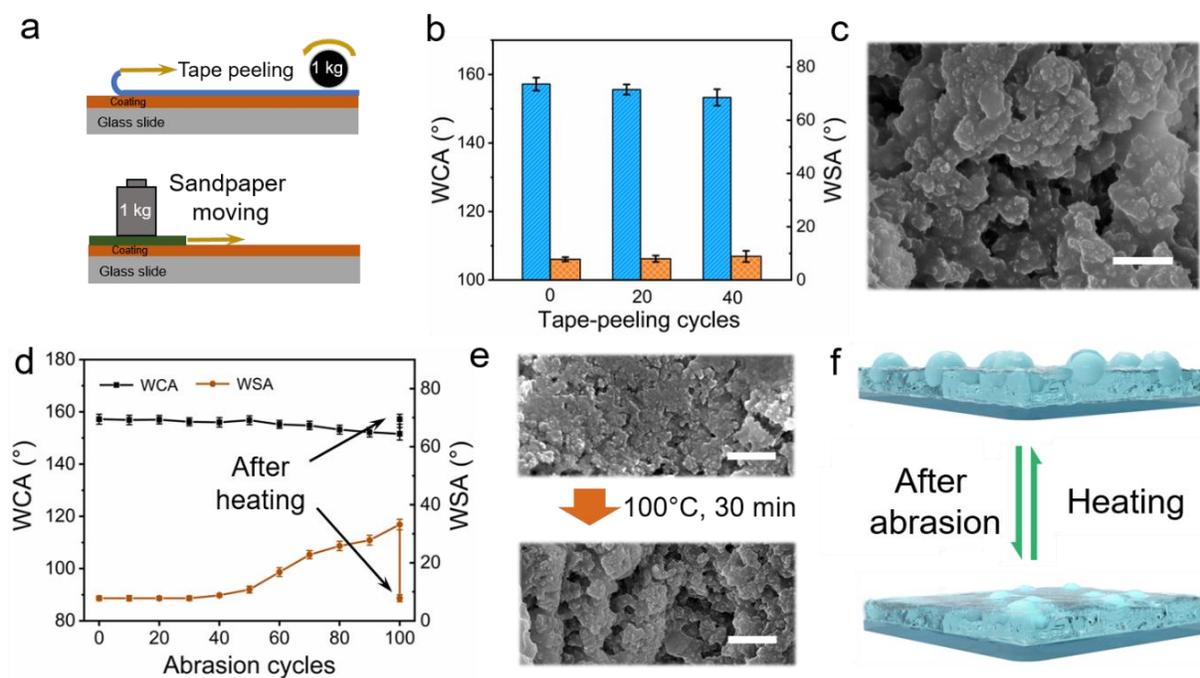


Figure 4. Mechanical robustness of the composite coatings. a) Schematic diagram of tape-peeling (up) and sandpaper abrasion (down) test. b) Changes of water contact and sliding angle with different cycles of peeling off test. c) SEM images of the coating after 40 times of peeling off test. d) Changes of water contact and sliding angle with different cycles of abrasion. e) SEM images of the coating after 80 times of abrasion (up) and after heating at 100°C for 30 min (down). f) Schematic diagrams of hierarchical structure of the coating surface after abrasion and heating. Scale bar is 2 μm .

Due to its high processibility, superhydrophobic paint can be applied to construct special pathway for fast water transport. As showed in Figure 5a, with the integration of mask, superhydrophobic paint was sprayed on the exposed area for water-repellency. After removing the mask, patterned wettability with designed hydrophilic pathways formed on the glass slide. As the shape of mask could be flexibly changed, various kinds water-guiding pathway could be formed (Figure 5b-c). Because the edge of the pathway was water-repellent, water was trapped in the hydrophilic area and moved along the designed pathway. This easily obtained droplet-guiding pathway was of great significance for programmable spatiotemporal manipulating of droplets on the surface.

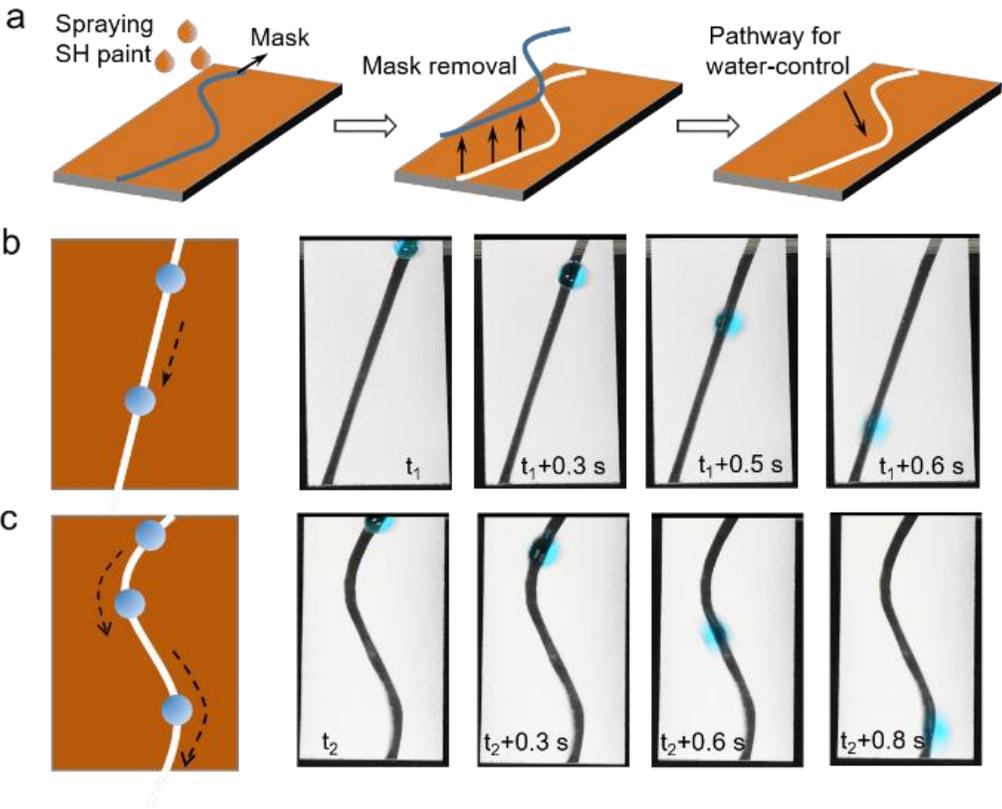


Figure 5. Dynamic control of water transport on the glass slide guided by designed pathways. a) Schematic diagram of the glass surface with patterned wettability. b, c) Oblique pathway and S-shape pathway for directional water transport.

4. Conclusion

In summary, we developed an easy-processible superhydrophobic paint by simply mixing supramolecular silicone polymers and silica nanoparticles in THF. Supramolecular silicone polymer with abundant hydrogen bonds and coordination bonds provided additional substrate binding and damage-healing properties, while silica nanoparticles contributed to enhancing surface roughness. The paint can be sprayed on various substrates to form porous coatings with enhanced water-repellency. This water-repellent coating exhibited remarkable mechanical stability and damaging-healing ability. Even after repeated tape-peeling, sandpaper abrasion and long-time underwater placement, surface still maintained superhydrophobicity with water contact angle higher than 150° and water sliding angle below 10° . Moreover, both topographical defects and surface chemistry can be recovered due to dynamic intermolecular crosslinking and chemical reorganization of the supramolecular polymers. Taking advantages of their high processibility, multifaceted robustness and inherent healing ability, the developed superhydrophobic coatings hold great promise for applications in liquid transport, oil-water separation, anti-icing and drag reduction.

Conflicts of interest

The authors declare they have no conflicts interest.

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