

Versatile Snail-Inspired Superamphiphobic Coatings with Repeatable Adhesion and Recyclability

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Abstract

Superamphiphobic surfaces with extreme repellency toward both water and oily liquids have been developed from various nanocomposites with fluorinated compounds. However, the inherent rigidity and low-surface-energy of these composites restrict their adhesion and practical application in adjusting the surface wettabilities of materials. Here we report a strategy to create hybrid superamphiphobic coating with rapid contact adhesion to various kinds of substrates, strong and controllable adhesive strength, unprecedented capability of mechanical deformations, facile removal, repeatable adhesion, and simple recyclization. Our approach, inspired by snail's ideal combination of hard shell and soft epiphragm, is versatile and industrially-viable because we use the hydrogel primer to bond the fluorinated nanoparticle finish and substrates. Considering the unique characteristics of these coatings as well as the wide range of available hydrogels and nanomaterials that can be used via this approach, we envision that this snail-inspired strategy will facilitate the development and large-scale production of superamphiphobic coatings.

Keywords: *superamphiphobic coatings, repeatable adhesion, recyclability, facile removal, stretchability*

Introduction

Superamphiphobic surfaces, which exhibit extreme repellency toward both water and oils with contact angles (CAs) greater than 150° and rolling angles (RAs) below 10°, are rarely found in nature but are highly desirable in many situations shaped by human activities.¹⁻³ Unlike superhydrophobic surfaces that only repel water, superamphiphobic surfaces exhibit remarkable applications in fields involving oily liquids or organic contaminants, such as drag reduction and anti-blocking of crude oil, anti-adhesion of cell and bacteria, self-cleaning of kitchen ventilators, protecting devices from fingerprints.⁴⁻⁸ Thus, the design and preparation of superamphiphobic surfaces have received considerable attention in both academia and industry.

Theoretically, the combination of low-surface-energy chemistry and nano/microscale hierarchical roughness (that hold air pockets in place) is the precondition to achieve superamphiphobic surfaces.⁹⁻¹¹ Accordingly, various low-surface-energy nanocomposites have been developed over a decade of intense research, typically using fluorinated compounds as low-surface-energy components and a diverse range of fillers that can provide the desirable surface roughness, including SiO₂,¹² TiO₂,¹³ ZnO,¹⁴ multi-walled carbon nanotubes,¹⁵ or raspberry-like polymer particles.¹⁶ Despite these accomplishments, an essential issue is how to achieve appropriate adherence between these existing composites and different kinds of substrates for practical application, which presents a considerable challenge because of their low-surface-energy and rigid nature.

Through efforts to address this inherent limitation, strong commercial adhesives have been reported to offer efficient bonding for superamphiphobic coatings.¹⁷ However, such intricate surface textures are highly

susceptible to mechanical wear, and the subsequent removal of the coating residues after prolonged use or severe abrasion would be difficult or could even cause damage to the substrates.^{18,19} In addition, the repeatable adhesion toward different substrates and a good degree of recyclability are highly desirable, considering the expensive fluorinated compounds and tediously fabricated nano-components that are necessarily used to prepare these materials.

Snails are a key example of a hybrid system existing in Nature as they possess an ideal combination of hard and soft materials, with a strong shell and repeatable adhesion epiphragm. Herein, we report a hybrid snail-inspired superamphiphobic coating (SS-coating, Figure 1), for the first time, that exhibit a rapid contact adhesion to various substrates, strong adhesive force, facile removal, repeatable adhesion, and easy recyclability. A versatile and scalable coating protocol was achieved by utilizing a hydrogel primer, which was designed with a loose network containing short crosslinked polymer chains in our previous work,²⁰ and a finish via spraying a *n*-hexane suspension of fluorinated nanoparticles (FNPs). The hydrogel was constructed using only simple commercially available monomers acrylamide and 2-hydroxyethyl methacrylate with an optimized preparation temperature. The FNPs was obtained by the surface modification of SiO₂ nanoparticles (SNPs) via *1H,1H,2H,2H*-perfluorodecyltrimethoxysilane (PFDTMS). *n*-Hexane was chosen as the solvent for the preparation of FNPs because of its immiscibility with water, so that it would have a negligible influence on the hydrogel primer and the bonding capability of the coating.

Experimental Section

Materials

Acrylamide (AAM), 2-hydroxyethyl methacrylate (HEMA), *N,N,N,N*-tetramethylethylenediamine (TEMED), *1H,1H,2H,2H*-perfluorodecyltrimethoxysilane (PFDTMS), hydrophilic SiO₂ nanoparticles (SNPs, with diameters of ~40 nm), *n*-hexadecane, diiodomethane, methyl blue, and tony red were purchased from Shanghai Macklin Chemical Reagent Factory. Ammonium persulfate (APS), acetic acid, and *n*-hexane were purchased from Tianjin Damao Chemical Reagent Factory. Hexamethylene diisocyanate-trimer (HT) was obtained from Shenzhen Zhibang Technology Co., Ltd. Crude oil (~1000 mpa·s⁻¹) was acquired from CNOOC Research Institute Co., Ltd. Canola oil were purchased from a local store and used as received.

Preparation of the hydrogel primers

AAM (7.10 g) and APS (0.10 g) were dissolved in 23.7 mL water and then mixed with HEMA (2.00 g) to obtain solution A. Meanwhile, HT (0.20 g) was added into 5 mL of anhydrous acetone and dissolved via ultrasonication to obtain solution B. 1.65 g of solution A was mixed with 40 μ L of solution B, which was followed by the addition of TEMED (5 μ L). Finally, the solution was placed into a mold (50 mm \times 25 mm) at 90 $^{\circ}$ C for 150 s and then reacted at ambient temperature for another 1 h to obtain the hydrogel primer.

Preparation of the FNPs suspension

SNPs (0.10 g) and acetic acid (0.15 g) were dispersed into 10 mL of *n*-hexane under ultrasonic treatment for 20 min. Subsequently, a solution of PFDTMS (0.10 mL) dissolved in 3 mL *n*-hexane was added dropwise. After continuous magnetic stirring for 3 h at 65 $^{\circ}$ C, the FNPs suspension was ready for the spraying treatments.

Preparation of the SS-coatings

The hydrogel primer (in the wet state) was applied onto various substrates, such as glass slides, wood plates, porcelain plates, and tin plates. Subsequently, different amount of the FNPs solution were loaded into an airbrush (0.25 mm nozzle diameter, 30 psi operating air) and sprayed onto the surface of the hydrogel (over an area of 1 \times 1 in²) from a distance of 10 cm. After spraying, the SS-coatings had been dehydrated for different lengths of time.

Characterization

The morphologies of the SNPs, FNPs, and SS-coatings were observed using a field-emission scanning electron microscope (FE-SEM, JSM-5600LV, JEOL). X-ray photoelectron spectroscopy (XPS, ESCALAB250XI,

Thermo Scientific, Waltham, MA) was employed to analyze the elemental compositions on the surfaces of the hydrogel primer and SS-coating. Fourier-transformer infrared spectroscopy (FTIR, Tensor 27, Bruker, USA) was performed to demonstrate particle surface modification. A contact angle goniometer (JC2000A, Zhongchen Powereach, Shanghai, China) was employed to measure CAs with 5.0 μL droplets, and RAs with 20 μL droplets. At least three different positions of the same sample were examined and the corresponding average value was taken as the reported CA or RA. The coating had been exposed to UV irradiation (UV aging test chamber, ZKHUS, Beijing) for various lengths of time to evaluate the UV resistance. The abrasion tests were carried out using an A20-339 abrasion test system (Chuangheng, China). A pressure of 4.5 kPa was applied over the cotton fabric (abrasion material) to increase the abrasion force, and the coating was repeatedly abraded with a cotton fabric with movements of 10 cm per cycle. The tape peeling tests were performed by pasting a 3M tape onto the coating, and a 100 g weight was rolled over this tape twice to ensure that the tape came into full contact with the coating, and the tape was subsequently peeled off. The shear adhesion strength was evaluated at a rate of 5 mm/min with the use of a universal tester (HZ-1007E, Dongguan Lixian Instrument Technology Co., Ltd., China). The samples were prepared by cutting hydrogels into 5 x 5 mm², fixing between two glass slides (25.4 x 76.2 mm²) and being compressed with a 100 g weight for 30 min, and subsequently curing in an oven at 50 °C for different lengths of time.

Results and Discussion

The characterization of the pristine SNPs and FNPs as well as the SS-coating are given in Figures S1-7 (Supporting Information), and the coating with a thickness of ~ 350 μm (hydrogel ~ 340 μm , FNPs ~ 10 μm), which exhibited CAs exceeding 150° for both water and oil as well as translucency with an optical transmittance exceeding 50 % at 500 nm, was selected for further investigation. The wettabilities of the glass substrate, hydrogel primer, and SS-coating toward water and *n*-hexadecane are shown in Figure 2a, which demonstrate the amphiphilicity of glass and the hydrogel in contrast with the superamphiphobicity of the SS-coating. In addition, the coating also displayed extreme repellency to hot water, highly acidic, highly alkaline, and salt-containing solutions, as well as various oily liquids including diiodomethane, canola oil, and crude oil, with CAs above 150° and RAs below 5° (Figure 2b). Moreover, this coating can be readily applied onto various other substrates besides glass, such as porcelain, wood, and metal, and exhibited similar outstanding superamphiphobicity (Figure 2c).

Thanks to the extreme repellency of the coating toward both water and oils, desirable self-cleaning performance can be achieved. As shown in Figures 2d and e, carbon black was readily removed from the coating surface via rinsing with water droplets or oil droplets without wetting the surface. Further investigations on the bouncing behavior of water and *n*-hexadecane are shown in Figures 2f-i, the jets of water and *n*-hexadecane readily bounced off the coating without wetting or even contaminating the surfaces.

The petroleum industry suffers from the strong adhesion of crude oil to most of the existing materials, including traditional oleophobic materials such as Teflon.²¹⁻²³ Figure 3a and Movie S1 (Supporting Information) provide a visual comparison of the coated and uncoated glass after their immersion in crude oil. Crude oil cleanly glided down the coated glass, while a persistent oil film remained on the uncoated glass. The coatings with anti-crude-oil-adhesion behavior and that can be readily applied onto different substrates could provide ideal candidates for the functionalization of many surfaces that are routinely exposed to crude oil, such as well shafts, pipelines, containers, analysis and refinery equipments.

Figure 3b shows a superamphiphobic pattern coating that was prepared by a mold and applied to a glass substrate. When the crude oil was poured on the surface of the pattern, the crude oil firmly adhered onto the surrounding glass, but the patterned regions remained clean (Movie S2 in Supporting Information). The rapid contact adhesion combined with the facile removal of our coating demonstrates a key advantage of this snail inspired technology for the creation of surfaces with temporary patterned wettability.

Nano/microscale textured structures are often sophisticated and prone to damage via mechanical deformation, which can limit the applicability of superamphiphobic coatings for flexible or stretchable materials and devices.^{24,25} By taking advantage of the outstanding flexibility and stretchability of the hydrogel component,

a minimum bending radius of less than 1 mm was reached for our coating (Figure 3c). Noteworthy, a limited variety of elongated surfaces that can only repel water have been achieved,²⁶⁻²⁸ while our SS-coatings retained its repellency toward both water and oily liquids even after the coating had been stretched by up to 500 %, when FNPs were sprayed onto the pre-stretched hydrogel coated silicone rubber (Figures 3d and e). Based on this unprecedented deformation capability of superamphiphobic coatings, we are currently exploring a higher stretchability and the surface functionalization of strain sensors and flexible batteries with various hydrogel structures and nanomaterials.

Generally, the intricate nano/microscale textures combined with their poor adhesion to substrates are mechanically weak, which makes robustness a central concern for superamphiphobic coatings.²⁹⁻³¹ The hydrogel component endows our SS-coating with both a rapid contact adhesion along with a strong adhesive force upon drying, as was confirmed by the lap shear strength tests. The shear strength increased from 2.3 ± 0.2 KPa for the initial hydrogel (~ 75 % water content) to 2.6 ± 0.2 MPa (~ 3.5 % water content) upon drying at 50 °C for 36 h, corresponding to a 1000-fold increase (Figures 4 a and b). Meanwhile, the hydrogel could also strongly adhere to other substrates including metal, wood, and porcelain (Figure 4 c). The coating could retain its superamphiphobicity despite knife scratching (Figure S8 in Supporting Information) and UV irradiation (Figure 4d). From the visual comparison of the insert image in Figures 4d and S9 (Supporting Information), the FNPs that directly applied on the glass substrate were easily removed via finger wiping, while the SS-coating exhibited only negligible change and maintained its superamphiphobicity. In addition, the coating could withstand 20 abrasion cycles while retaining its superhydrophobicity, although a reduction of the oil repellency was observed (Figure 4e). The superamphiphobicity did not exhibit significant change after 15 tape peeling cycles, and the superhydrophobicity was retained after 25 cycles (Figure 4f). These mechanical tests suggest that this coating provide a promising robustness with respect to the existing superamphiphobic surfaces.^{17,32-34}

By utilizing this dramatic change of wet and dry adhesive strength in a single hybrid material, and subtly introducing the water absorption and dehydration through the coating cross-section, the coating permits strong bonding while still offering facile removal and repeatable use for various substrates. As shown in Figure 5a, the coating was readily peeled from a glass substrate after it had undergone targeted water absorption with a syringe (across the cross-section of the coating), and it could then be re-applied onto a wood plate to endow superamphiphobicity. The shear strength remained essentially unchanged after each removal and re-adhesion cycle, thus demonstrating the repeatable adhesion capabilities of the coating (Figure 5 b).

On the other hand, the separation of this hybrid material could be achieved by simply immersing the coated glass in water for ~ 2 h. The water would penetrate through the coating cross-section to yield a piece of swollen hydrogel and a floating layer of detached FNPs, thus it affords us a simple way to achieve the collection of these different components (Figure 5c). Subsequently, the collected hydrogel and FNPs could be used again to endow various substrates with superamphiphobicity (Figure 5d).

Conclusion

In summary, a versatile and industrially-viable snail-inspired strategy reported herein provides a hybrid superamphiphobic coating with a combination of unique characterizations including rapid contact adhesion to different substrates, strong and controllable bonding strengths (~ 2.3 KPa to ~ 2.6 MPa), facile removal, repeatable adhesion, stable liquid repellency with unprecedented stretchability up to 500 %, and simple recycling with uncompromised properties. These combined properties can be leveraged to meet the demands of numerous applications, and should also provide an avenue for reducing costs and minimizing environmental footprint of superamphiphobic materials. The outstanding anti-crude-oil-adhesion and applicability for different substrates provide an attractive means improving the efficiency for the crude oil extraction, transportation, storage, and processing. The rapid contact adhesion combined with the facile removal demonstrates a key advantage endowing surfaces with temporary patterned wettability. In addition, the unprecedented tolerance to mechanical deformation exhibits remarkable potential for the surface functionalization required for the rapid advancements of stretchable materials and devices in fields of information technology and bio-

technology. The snail-inspired insight gained from this work is adaptable for developing superamphiphobic coatings utilizing a broad variety of available hydrogels and nanomaterials as precursors possessing a range of different physical and chemical properties.

Acknowledgments

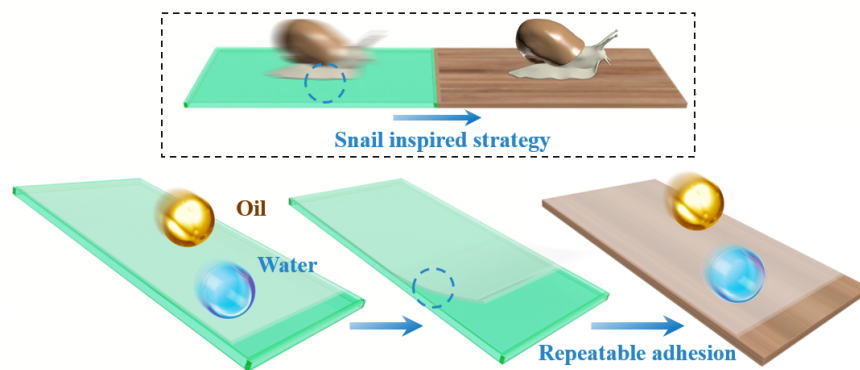
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Figure 3. Anti-crude-oil-adhesion, patterned wettability, and unprecedented stretchability. Behavior of crude oil on the coated and uncoated glass (a). The patterns retained clean after crude oil had been poured over them (b). The minimum bending radius for a coated tin plate (c). Schematic illustration showing the fabrication of highly stretchable superamphiphobic materials (d). Stable superamphiphobicity against both water and *n*-hexadecane even under stretching of 500 % (e).

Figure 4. Robustness. The influence of the dehydration time at 50 °C on the shear strengths (a) and water contents (b) of hydrogel. The shear strengths of the hydrogel on tin, glass, wood, and porcelain substrates after dehydration at 50 °C for 36 h (c). Changes in the CAs and RAs of coated glass with various time of UV irradiation (d). The insert photographs show the effects of finger friction on the FNP film and the SS-coating. Changes in the CAs and RAs of the coated glass after it had been subjected to abrasion tests (e) and tape peeling tests (f). The inset diagrams in e and f illustrate the methods employed for the respective tests.

Figure 5. Repeatable adhesion and recyclability. Photographs taken during various stages of the removal from glass and re-adhesion to wood process for the coating (a). The shear strength of a coating that had been re-adhered to the same glass substrate for 3 cycles, and the strength was regenerated during each cycle via dehydration at 50 °C for 36 h (b). Photographs taken during the key stages of the coating recycling process (c). The recycled coating exhibited negligible changes in its superamphiphobicity (d).

Figures

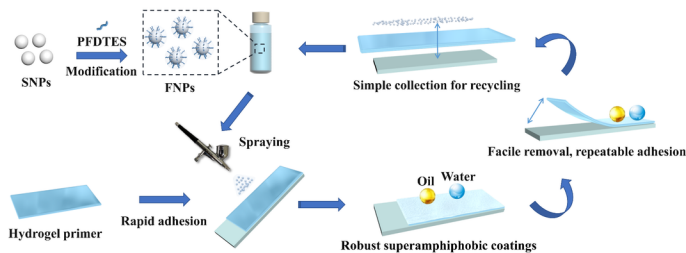


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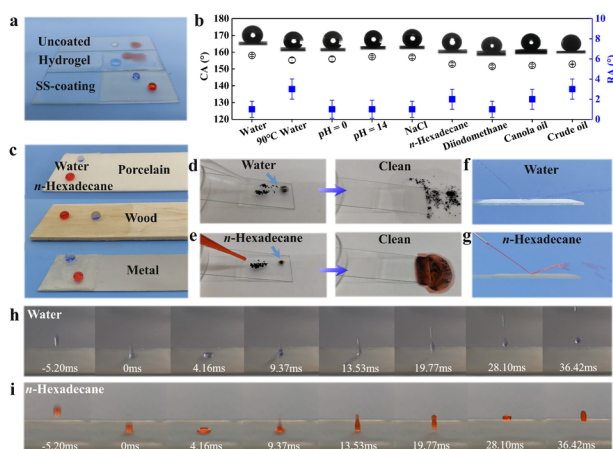


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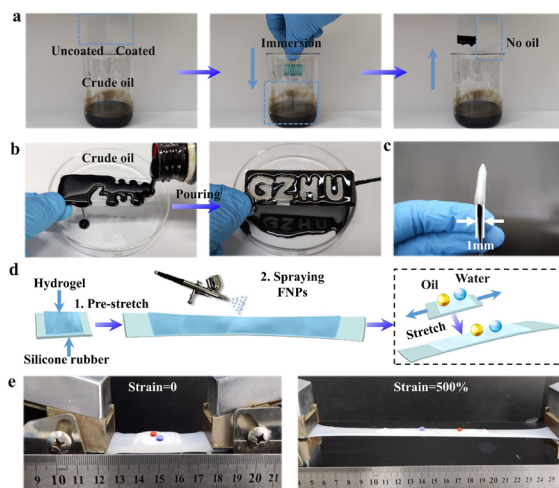


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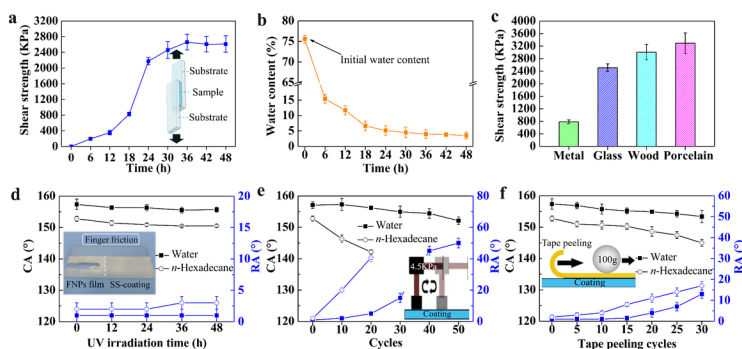


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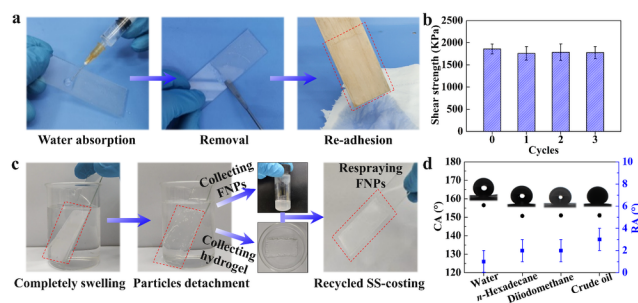


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