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Fabrication of All-Water-Based Self-Repairing Superhydrophobic Coatings Based on UV-Responsive Microcapsules

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Superhydrophobic coatings that are also self-healing have drawn much attention in recent years for improved durability in practical applications. Typically, the release of the self-healing agents is triggered by temperature and moisture change. In this study, UV-responsive microcapsules are successfully synthesized by Pickering emulsion polymerization using titania (TiO_2) and silica (SiO_2) nanoparticles as the Pickering agents to fabricate all-water-based self-repairing, superhydrophobic coatings. These coatings are environmentally friendly and can be readily coated on various substrates. Compared to conventional superhydrophobic coatings, these coatings can regenerate superhydrophobicity and self-cleaning ability under UV light, mimicking the outdoor environment, after they are mechanically damaged or contaminated with organics. They can maintain the superhydrophobicity after multiple cycles of accelerated weathering tests.

1. Introduction

Superhydrophobic surfaces, which have a water contact angle (WCA) greater than 150° and a water droplet sliding angle less than 10°,[1] have numerous potential applications, including self-cleaning,[2] anti-corrosion,[3] anti-icing,[4] drag reduction,[5] and non-wetting fabrics.[6] However, their durability in an outdoor environment is often questionable, thus, limiting their practical implementation.[7] Despite many advances in recent years it remains challenging to improve environmentally durability and mechanically robustness of superhydrophobic coatings,[6b,8] since surface topography required to achieve superhydrophobicity is intrinsically weak mechanically. Therefore, "self-repairing" strategy is attractive to realize the long-term durability of superhydrophobic surfaces.[6c,9] Li et al. have demonstrated a self-healing, superhydrophobic coating containing perfluorooctanesulfonic acid lithium salt (PFOS) or fluoroalkyl silane (FAS) in their porous structures.[7b,10] Once the top layer was decomposed or scratched, the preserved PFOS or FAS would migrate toward the surface to regenerate superhydrophobicity in the presence of humidity. Wang et al. have fabricated a self-healing, superhydrophobic, and superoleophobic fabric via deposition of a mixture of fluorinated-decyl polyhedral oligomeric silsesquioxane (FD-POSS) and hydrolyzed FAS on surface.[11] The fabrics could maintain superhydrophobicity even after 100 cycles of the plasma-and-heat treatment. Manna et al. have demonstrated a repairable superhydrophobic porous polymer film via layer-by-layer assembly of branched poly(ethylenemine) and poly(vinyl-4,4-dimethylazlactone).[9b] Upon immersion in water, the damaged surface could restore its topographic features and fully recover superhydrophobicity. Esteves et al. have created a robust superhydrophobic coating by casting of a dispersion consisting of dual-sized silica nanoparticles and fluoroalkyl-terminated polymeric dangling chains. The coating spontaneously recovers the surface chemical compositions by reorientating the dangling chains toward the newly created surfaces after mechanical damage.[12] Despite these advances, most systems release their encapsulated self-healing agents triggered by temperature or moisture changes. None has reported light-induced self-healing superhydrophobic surfaces. Indeed, light-induced self-healing phenomena are common in nature. Hence, it will be energy efficient to design an artificial superhydrophobic surface using natural lighting in an outdoor environment. In addition, all the self-healing superhydrophobic coatings reported in literature so far use pungent organic solvents to dissolve hydrophobic substances, drawing environmental and safety concerns during large-scale production and applications.[13] This is because it is very difficult to realize waterborne superhydrophobic coatings.

In this paper, we have successfully fabricated all-water-based self-repairing superhydrophobic coatings based on UV-responsive microcapsules (referred as U-capsules). They offer several distinct advantages, including: i) It is the first time that UV-responsive capsules have been synthesized by Pickering emulsion polymerization using titania (TiO_2) and silica (SiO_2) nanoparticles as the Pickering agents; ii) Superhydrophobicity

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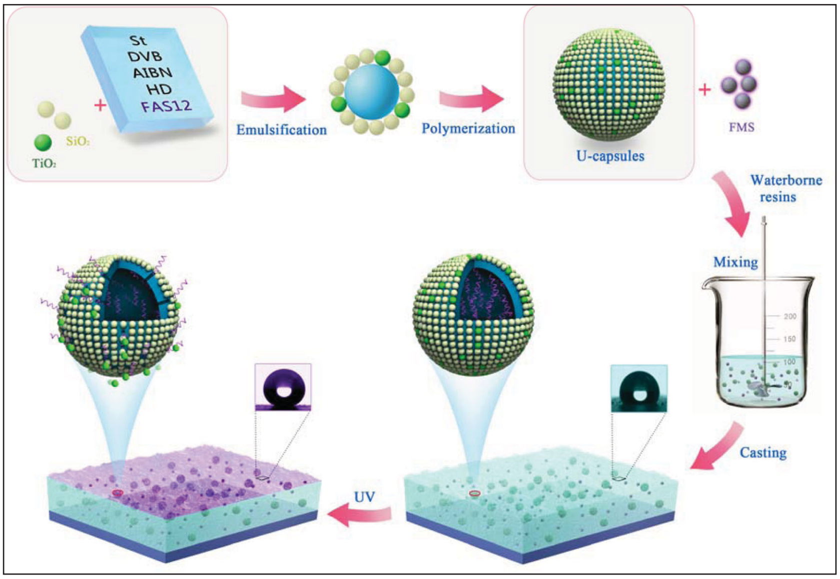


Scheme 1. Schematic illustration of the preparation of all-water-based self-repairing superhydrophobic coatings based on U-capsules.

can be recovered under UV light after mechanical damage or contamination by organics; iii) They are waterborne and environmentally friendly.

2. Results and Discussion

2.1. Preparation of UV-Responsive Microcapsules

As shown in **Scheme 1**, fluoroalkyl silane (FAS12)-loaded U-capsules were synthesized via Pickering emulsion polymerization of styrene (St), divinylbenzene (DVB), 2,2′-azobis(2-methylpropionitrile) (AIBN), hexadecane (HD), FAS12, and water using modified SiO_2/TiO_2 nanoparticles as the Pickering emulsifiers. Because TiO_2 nanoparticles are known for their photocatalytic property under UV irradiation for organic compounds, the as-obtained U-capsules could release hydrophobic FAS12 molecules under UV light through decomposition of the polymers in the microcapsules. They also possessed good miscibility with waterborne resins, including polysiloxane and modified nanosilica. When the U-capsules were mixed with waterborne resins and applied on a substrate, followed by UV irradiation, FAS12 was released. Together with rugged surface from the microcapsules covered with a dense layer of SiO_2 and TiO_2 nanoparticles (see scanning electron microscope (SEM) and transmission electron microscope (TEM) images shown in **Figure 1**a,b), superhydrophobic surface was achieved.

The coverage of SiO_2 and TiO_2 nanoparticles was further confirmed by energy-dispersive X-ray spectroscopy (EDX) analysis (Figure 1c). Dynamic light scattering (DLS) measurement showed that the mean diameter of nanoparticles was ≈170 nm (Figure 1d), consistent with SEM and TEM images. To better observe the internal structures of the capsules, we prepared larger ones (1–2 μm) using less SiO_2 and TiO_2 nanoparticles as the Pickering emulsifiers, which clearly showed hollow structures (Figure S1, Supporting Information). This is because both HD and FAS12 are non-solvents for the polymers, therefore, interfacial tension drives the St–DVB copolymers toward the interface of the colloidosomes, forming the shell of the hollow capsules.[14] When these microcapsules were irradiated by UV light, some FAS12 molecules were released apparently due to decomposition of the polystyrene (PS) shell, which was confirmed by Fourier transform infrared spectroscopy (FTIR) (Figure S2, Supporting Information). When no TiO_2 nanoparticles were used as the co-Pickering agent, no FAS12 was released.

2.2. Preparation of Waterborne Self-Repairing Superhydrophobic Coatings

When these U-capsules were dispersed into waterborne polysiloxane latex, the as-prepared coating surface was hydrophilic (WCA: 85.6°), regardless of the ratios of U-capsules to

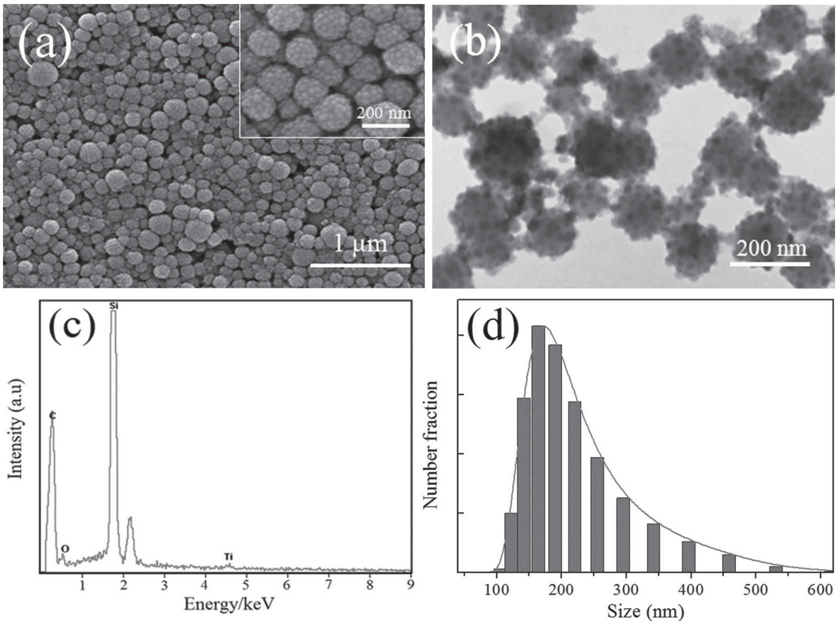


Figure 1. a,b) SEM and TEM images of U-capsules. c) EDX spectrum of U-capsules. d) Size distribution of U-capsules measured by DLS.

polysiloxane. When heptadecafluoro-1,1,2,2-tetradecyl trimethoxysilane (FAS17)-modified SiO_2 (FMS) were added into this system, the dried coating surface became hydrophobic with a WCA of 119.3° and a sliding angle of 65° at 25 wt% of FMS (Figure S3, Supporting Information). Further increase of the FMS amount or changing the ratios of U-capsules/polysiloxane/FMS did not increase WCA. Very interestingly, however, when the dried coating sample was put in a QUV accelerated weathering tester for 96 h, superhydrophobic surface was obtained with a WCA increased to 152° and a water droplet sliding angle decreased to 5.9° (**Figure 2**a,b). For comparison, we also investigated other capsules, including pure U-capsules, U-capsules plus unmodified silica, and FMS plus capsules without TiO_2 as co-Pickering agent and measured the WCAs of their nanocomposite coatings before and after UV irradiation. As shown in Figure 2c, no change in WCA was found for FMS plus capsule without TiO_2-based nanocomposite coating, but ≈30° increase in WCA was observed for these U-capsule-based nanocomposite coatings after QUV accelerated weathering treatment. The results clearly suggest the superhydrophobic surface is achieved only after release of hydrophobic FAS12 molecules under UV irradiation. The UV-irradiation time to reach superhydrophobicity could be further adjusted by the mass fraction of TiO_2 during the synthesis of the U-capsules. Typically, the more TiO_2 nanoparticles, the shorter UV irradiation time was needed. The coating is versatile. However, if only TiO_2 was used the Pickering emulsifier, the as-obtained U-capsules would release FAS12 under UV light too quickly to maintain a good self-repairing durability of coatings. Therefore, addition of SiO_2 nanoparticles was necessary to adjust the releasing rate of FAS12 and fine-tune the final self-repairing durability of the coatings. Furthermore, we showed that superhydrophobic surfaces could be formed on different substrates, including paper, glass, tin, polypropylene, and wood (Figure S4, Supporting Information). We note that after immersing the coating in water for a week, it lost superhydrophobicity due to the enrichment of hydrophilic molecules and the loss of hydrophobic FAS12 molecules on the surface. Nevertheless, the surface topography did not change (Figure S5, Supporting Information). When re-exposed to UV light, surface recovered superhydrophobicity, indicating release of the hydrophobic FAS12 molecules from the U-capsules again (Figure S6, Supporting Information).

To further proof the UV irradiation effect on the formation of superhydrophobic surfaces, we examined the surface morphologies of the as-obtained coatings by SEM. As shown in Figure 2d, a dual-scale roughness appeared on the surface consisting of large irregular microscale aggregates (2–8 μm), assembled from U-capsules, and nanoapophysis (20–200 nm) clearly attributed to TiO_2 and SiO_2 nanoparticles.[15] After accelerated weathering test for 96 h, no obvious change of the surface topography was observed (Figure 2e), further confirming that superhydrophobicity of the nanocomposite coatings was resulted from the UV-induced rupture of U-capsules, releasing low surface energy FAS12 molecules.

2.3. Durability under UV Irradiation

The atomic composition of surfaces as a function of UV irradiation time was measured by X-ray photoelectron spectroscopy (XPS). It revealed that the surface F concentration increased as a function of UV-irradiation time (**Figure 3**a), another evidence

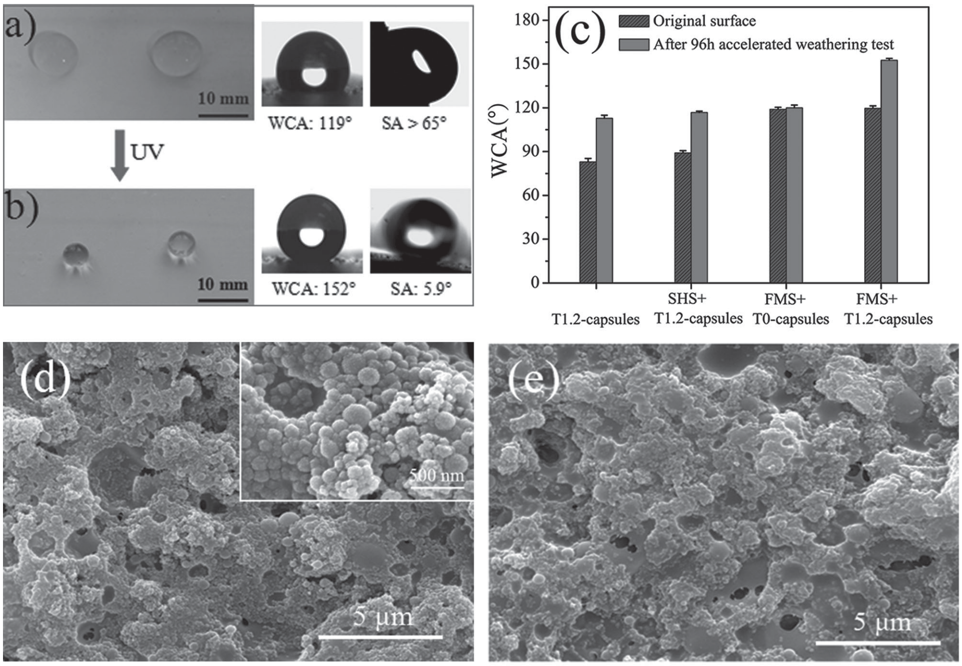


Figure 2. Photographs of water droplets sitting on the coated samples before a) and after b) UV irradiation in an accelerated weathering tester for 96 h. c) Change of WCA on various nanocomposite coatings before and after UV irradiation in the accelerated weathering tester for 96 h. d,e) Top-view SEM images of the coating before d) and after e) 96 h accelerated weathering test.

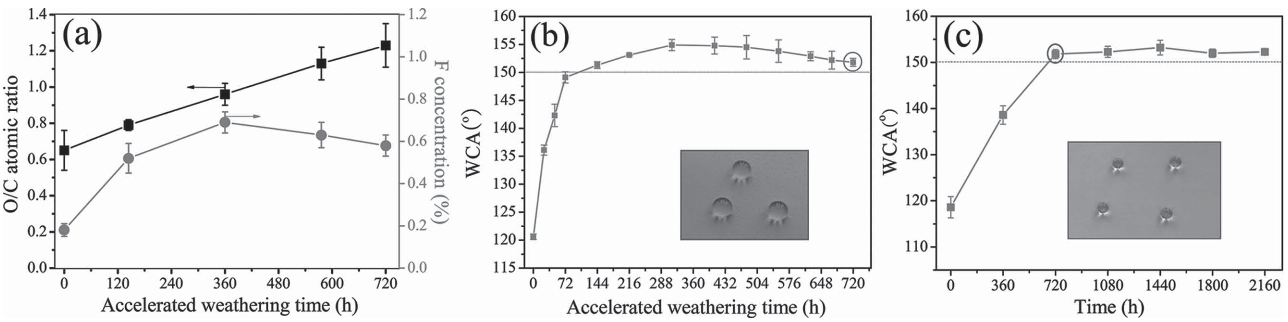


Figure 3. a) Surface O/C compositions of the coating as a function of accelerated weathering time. b) WCAs of the coating versus the accelerated weathering time. Inset: the water droplets on the superhydrophobic coating after prolonged weathering for 720 h. c) WCAs of the coating panel versus outdoor exposure time. Inset: the water droplets on the coating panel after outdoor exposed for more than 720 h. Coating: T1.2-capsules/polysiloxane/FMS.

that the FAS12 molecules gradually enriched the top layer of the coating surface. Moreover, the O/C atomic ratio increased significantly, from 0.4 to 1.35, after accelerated weathering treatment for 720 h due to the photo-catalyzed degradation of PS by TiO_2 nanoparticles. These results undoubtedly show that slow release of FAS12 molecules from U-capsules under UV-irradiation allows for a long-term superhydrophobic surface. Again, the surface morphology did not change; neither chalking nor reduction of film thickness was observed (Figures S7 and S8, Supporting Information). Owing to the release of FAS12 molecules from U-capsules, the WCA of surface increased to 154.3° with the UV irradiation time until 360 h. Prolonged UV irradiation could lead to a small loss of FAS12 molecules, thus, decreasing the WCA. Nevertheless, the coating surface kept WCA > 150° after accelerated weathering treatment for 720 h (Figure 3b). Supporting this, we showed that the coating remained superhydrophobic after more than 2160 h in an outdoor environment (Figure 3c).

2.4. Self-Regeneration of Superhydrophobic Surface upon Mechanical Damage

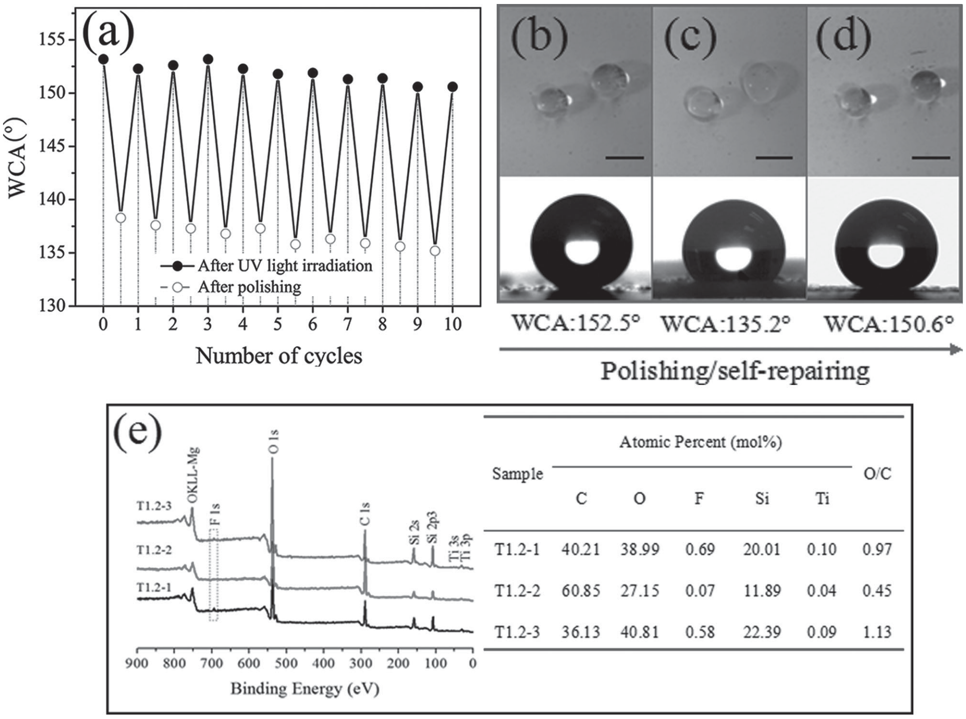
Besides UV degradation, physical abrasion is another challenge to artificial superhydrophobic surfaces, which will not only destroy the hierarchical structures but remove the hydrophobic substances from the top layer of the surfaces.[7] To evaluate the influence of mechanical abrasion and the self-repairing ability of the superhydrophobic coatings in our system, we manually rubbed the superhydrophobic surface using abrasive sandpaper under 20 kPa pressure. The WCA decreased and the sliding angle increased as shown in **Figure 4**a. Upon UV irradiation, the coated surface could recuperate its superhydrophobic state even after ten cycles of polishing and accelerated weathering (see Figure 4b–d). Similarly, the surface morphologies did not display any obvious change after UV irradiation (Figure S9, Supporting Information), again supporting that the self-repairing ability of the superhydrophobic coatings was the result of UV-induced release of FAS12. As shown by XPS measurement (see Figure 4e), the UV-irradiated surface had an atomic surface composition comparable with the pristine one. After polishing, the composition of F decreased sharply (from 0.69% to 0.07%), but was nearly recovered after UV-irradiation to 0.58%. Along with the change of F composition was the considerab increase of the O/C atomic ratio after UV irradiation, from 0.45 to 1.13.

2.5. Recovery of Superhydrophobic Surface after Oil Pollution

We note that superhydrophobic surfaces do not necessarily repel oily organic contaminants.[7a,16] Therefore, we further examined the resistance of the superhydrophobic coating to organic contaminants, using oleic acid and methyl blue (MB) as the model pollutants. As shown in **Figure 5**a–c, the WCA of superhydrophobic coating decreased from 152.8° to 59.2° when a thin layer of oleic acid was cast on the surface. However, after UV irradiation in the accelerated weathering test chamber for 36 h, the coating surface recovered superhydrophobicity (151.3°). After twelve cycles of oleic acid casting and UV illumination in the accelerated weathering tester, the coating remained superhydrophobic (Figure 5d). As control experiments, we prepared capsules without TiO_2 and mixed FMS with polysiloxane latex. As seen in Figure S10, Supporting Information, after casting oleic acid on surface, it became hydrophilic and remained hydrophilic after UV irradiation. It is clear that TiO_2 nanoparticles in the U-capsules played an essential role to photocatalytically decompose oleic acid, and therefore endowing the coating's resistance to organic contaminants. When the U-capsules contained no FAS12, although its coating also recovered its original hydrophobicity, the recovery rate was much slower than those containing FAS12. When this superhydrophobic film was put into MB solution and irradiated by UV light in the accelerated weathering tester, the blue color gradually faded and finally disappeared completely, as shown in Figure 5e, again confirming the photocatalytic response of the coating.

3. Conclusion

In summary, FAS12-loaded UV-responsive microcapsules were successfully synthesized via Pickering emulsion polymerization, and easily dispersed into waterborne polysiloxane



Sample	Atomic Percent (mol%)					O/C
	C	O	F	Si	Ti	
T1.2-1	40.21	38.99	0.69	20.01	0.10	0.97
T1.2-2	60.85	27.15	0.07	11.89	0.04	0.45
T1.2-3	36.13	40.81	0.58	22.39	0.09	1.13

Figure 4. a) Change of WCAs for the superhydrophobic coatings as a function of repeated polishing and accelerated weathering cycles. b–d) Photographs of water droplets and contact angles on the superhydrophobic surfaces. b) Original sample. c) After 10 cycles. d) After accelerated weathering test for 84 h. Scale bars: 5 mm. e) XPS scans of the coated surfaces (T1.2–1, original; T1.2–2, after ten cycles; T1.2–3, after accelerated weathering test for 84 h). Atomic compositions of the coating, T1.2-capsules/polysiloxane/FMS.

latex. After spray coating the microcapsules on an aluminum plate, followed by UV irradiation, superhydrophobic surfaces were obtained attributed to the release of FAS12 from the partially ruptured capsules as confirmed by XPS studies. The coating was versatile, besides aluminum, it could also be applied to paper, glass, tin, polypropylene, and wood to achieve superhydrophobicity. Moreover, the surface could recover its superhydrophobic and self-cleaning ability under UV light even after it was mechanically damaged or contaminated with organics. The coatings reported here are environmentally friendly and especially attractive for outdoor applications. We believe that the TiO_2-induced UV responsive microcapsules reported here can be further extended to prepare other waterborne, self-healing coatings with temperature-, moisture-, or multi-responsiveness.

4. Experimental Section

Materials: Styrene (St, ≥99%), divinylbenzene (DVB, ≥80%), 2,2′-azobis(2-methylpropionitrile) (AIBN, ≥99%), hexadecane (HD, ≥98%), 3-isocyana-topropyltriethoxysilane (IPTS, ≥95%), and *t*-octylphenoxypolyethoxyethanol (Triton X-100, biochemical grade) were purchased from Aladdin Chemical Reagent Co. (China). Ammonia solution ($NH_3{\cdot}H_2O$, 25 wt%), acetic acid (≥99.7%), ethanol (≥99.7%), and dibutyltin dilaurate (DBTDL, ≥95%) were purchased from Sinopharm Chemical Reagent Co. (China). St and DVB were distilled under vacuum before use and the other reagents were used as received. Dodecafluoroheptyl-propyl-trimethoxysilane (FAS12, $C_{13}H_{18}F_{12}O_3Si$) was purchased from Xeogia Fluorine-Silicon Chemical Co., Ltd. (China). (Heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane (FAS17) was purchased from Nanjing Daoning Chemical Co., Ltd. (China). Aqueous silica sol (30 wt%, pH: 6–8, diameter: 20 nm) was supplied by Zhangjiagang Churen New Materials Technology Co., Ltd. (China). Nano-titania dispersion (ACTiV^{TM} S5–300B) was supplied by Cristal. SiO_2 nanoparticles (SHS-1, hydrophilic, primary size: 20 nm) were purchased from Shanghai Shanghui Nanotechnology Co., Ltd. (China). Polysiloxane latex (SIRES BS-45, solid content: 54 wt%) was purchased from Wacker Chemicals (Germany). Deionized water was used throughout the whole experiments.

Modification of Silica and Titania Nanoparticles: 6.5 g Triton X-100, 2.5 g IPTS, and DBTDL were added into a 50 mL three-neck flask and mechanically stirred at 50 °C for 20 h under nitrogen atmosphere to obtain Triton X-100-IPTS (T-IPTS). Then 2.8 g SiO_2 sol (solid content, 30 wt%; pH 6–8; diameter: 20 nm) was added to 100 mL water under agitation. Subsequently, 0.05 g T-IPTS was dropped to the dispersion and the pH value of the dispersion was adjusted to 8 via dropping diluted ammonia solution at room temperature. The reactant was magnetically stirred at 65 °C for 24 h to obtain the modified SiO_2. The modified TiO_2 nanoparticles were prepared with the same procedure without adjusting the pH value of the dispersion.

Synthesis of UV-Responsive Microcapsules: In a typical process, 200 mL aqueous solution dispersed with Triton X-100-tethered silane coupling agent-modified-SiO_2 (20 nm in diameter) and TiO_2 nanoparticles (40 nm in diameter) (total nanoparticles mass: 0.9 g) were mixed with the oil phase (2 g of St, 0.04 g of DVB, 0.6 g of FAS12, 0.1 g of HD, and 0.06 g of AIBN) in a 250 mL glass beaker. This mixture was emulsified using a FLUKO homogenizer at 12000 rpm for 5 min, and then poured into a 250 mL three-neck flask and deoxygenated by bubbling with N_2 for 30 min. The Pickering emulsion was then heated to 70 °C and mechanically stirred for 24 h to produce UV-responsive microcapsules with polystyrene shells. The as-obtained U-capsules were separated by centrifugation at 10000 rpm for 10 min and then dispersed in water

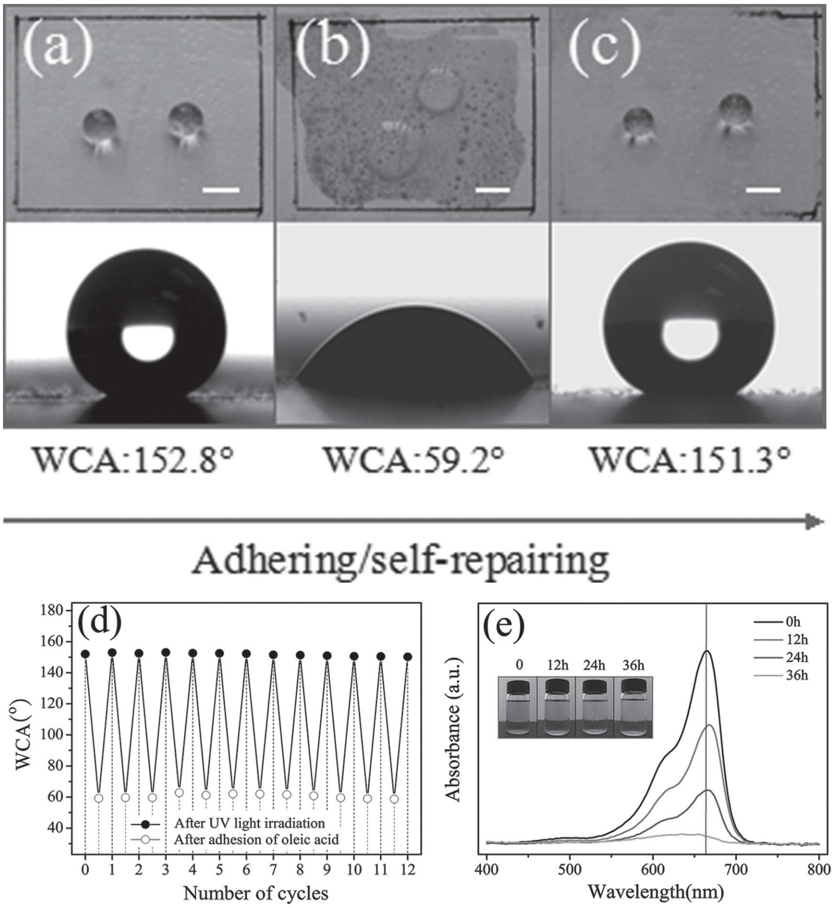


Figure 5. a–c) Photographs of water droplets and contact angles on the superhydrophobic surfaces. a) Original. b) Spread with oleic acid. c) After accelerated weathering test for 36 h. Scale bars: 5 mm. d) Change of the WCAs for the superhydrophobic surfaces as a function of the cycle number of the oleic acid spreading and accelerated weathering. e) UV–Vis spectra of the aqueous solutions (dyed with methylene blue) at different UV-irradiation time in the presence of the superhydrophobic coatings. Coating: T1.2-capsules/polysiloxane/FMS.

with a solid content of 20 wt%. The U-capsule prepared at the TiO_2/SiO_2 mass ratios of 5:95 was designated as T1.2-capsules. U-capsules with TiO_2/SiO_2 mass ratios such as 10:90 and 15:85 could also be prepared using the same process. For control experiments, two microcapsules, including one without TiO_2 nanoparticles and the other without FAS12, were synthesized and defined as T0- and F0-capsules, respectively.

Preparation of Aqueous Dispersion of FMS Nanoparticles: Briefly, 3 g SHS-1, 150 g water, and 0.75 g ammonia were charged into a 250 mL round-bottom flask equipped with a stirrer, a thermocouple, a condenser, and a heating mantle. This mixture was stirred for 30 min and then added by 0.1 g FAS17 and 10 g ethanol. The reaction was allowed to run under constant stirring at 65 °C for another 24 h. The FAS17-modified silica nanoparticles (FMS) were then collected by centrifugation (8000 rpm, 10 min), and then re-dispersion in distilled water for further use. FTIR displayed two absorption peaks at 2983 and 2916 cm^{-1} attributed to antisymmetric and symmetric C–H stretching, confirming the successful grafting of FAS17 to the silica nanoparticle surface.

Preparation of Waterborne Self-Repairing Superhydrophobic Coatings: Typically, 5 g polysiloxane latex, 4.5 g U-capsule aqueous dispersion (solid content: 20 wt%), and 2.8 g aqueous dispersion of FMS nanoparticles (solid content: 40 wt%, see Supporting Information) were mixed at 500 rpm for 10 min. The coatings were then cast on aluminum plates using a drawdown rod (120 μm) and dried at 80 °C for 20 min. For comparison, four control coatings were also prepared from T1.2-capsules, T1.2-capsules/SHS (SHS: unmodified SiO_2 nanoparticles), T0-capsule/FMS, or F0-capsules/FMS following the same procedure.

Characterization: FTIR measurements were carried out with a Nicolet Nexus 470 spectrometer (Thermo Fisher, USA) with a resolution of 0.5 cm^{-1} for 32 scans. The dried samples were blended with KBr to prepare pellets. The morphologies of the microcapsules were characterized by scanning electron microscope (SEM Philips XL 30) at an accelerating voltage of 30 kV and transmission electron microscope (TEM Hitachi H-800, Hitachi Corp, Japan) at an accelerating voltage of 10 kV, respectively. The size of microcapsules was determined by dynamic light scattering (DLS) method using Nano-ZS90 (Malvern, UK). Elemental analysis was performed by energy-dispersive X-ray spectrometer (EDX) within SEM. Water contact angles (WCAs) and sliding angles (SAs) were measured by OCA15 contact angle analyzer (Dataphysics, Germany) averaged over 5 fresh spots using a 5 μL deionized water droplet. The accelerating weathering tests were carried out in a QUV accelerated weathering tester (QUV/se, Q-Panel Co., Ltd., USA) with UV lamps at wavelength of 310 nm. The samples were exposed to UV-irradiation (intensity of 0.71 W m^{-2}) at 60 °C for 4 h, followed by condensation at 50 °C for 4 h. UV irradiation for photocatalytic degradation was carried out at room temperature using a 150 W high-pressure mercury lamp as the irradiation source (365 nm). The surface composition of the coating film was measured by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ECSA) using Al K radiation at a 90° take-off angle. All the binding energy values were calibrated using the reference peak of C_{1S} at 284.6 eV. The abrasion resistance of the superhydrophobic surfaces was evaluated by dragging a piece of 1500-mesh sandpaper under 1 kg weight in one direction with a speed of 1 cm s^{-1}. The contact area between the sandpaper and the underlying superhydrophobic coating was 2.25 cm × 2.25 cm. The resistance of the coating to oily contaminants was examined using oleic acid as the model pollutant. A thin layer of oleic acid was sprayed on the coating surface, which was then put into the accelerated weathering tester. The WCAs were measured after 12 h interval. The photocatalytic performance was evaluated by the decolorization of the methylene blue (MB) solution that was prepared by dissolving MB in the mixture of water and alcohol (1:1 in volume ratio). A piece of coated aluminum sheet (10×5 cm^2) was immersed in 15 mL MB solution (0.02 mmol L^{-1}) and then put into the accelerated weathering tester. The color change of the solution was monitored by UV–vis absorption spectra using a U-4100 spectrophotometer (Hitachi, Japan) at a certain time interval. Outdoor exposure experiments were carried out from 26 February 2014 to 27 May 2014. All the coated aluminum panels were mounted on an outdoor exposure rack ≈200 m away from the street on a rooftop facing south with an tilting angle of 45°. The change of WCA was periodically recorded.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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