

Supporting Information

Facile Fabrication of Self-Repairing Superhydrophobic Coatings

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Experimental details

Materials

Polystyrene (PS, General purpose, $M_w = 2 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$) and butyl acetate were purchased from Aladdin Reagent Co., Ltd. α,ω -Bis(hydroxypropyl)-terminated poly(2,2,3,3,4,4,4-heptafluorobutylmethylsiloxane) (PMSF, $M_w=8000\text{g}\cdot\text{mol}^{-1}$) was obtained from Guangzhou Kang-Gu-Jia Chemical Technology Co., Ltd. (Heptadecafluoro-1,1,2,2- tetrahydrodecyl) trimethoxysilane (FAS-17) was purchased from Nanjing Daoning Chemical Co., Ltd. TiO_2 nanoparticles (P25, primary size: 27 nm) were purchased from Degussa. SiO_2 nanoparticles (SHS-1, hydrophilic, primary size: 20 nm) were purchased from Shanghai Shanghui Nanotechnology Co., Ltd. SiO_2 nanoparticles (TS-530, hydrophobic, primary size: 12 nm) was supplied from Shanghai Cabot Chemical Co., Ltd.

Modification of silica nanoparticles

Briefly, 3 g of SHS-1, 60 g of ethanol and 0.75 g of ammonia were charged into a 250 mL round-bottomed flask equipped with a stirrer, a thermocouple, a condenser and a heating mantle. The mixture was stirred for 30 min and then 0.3 g of FAS was added to the flask. The reaction was allowed to continue under constant stirring at temperature $65 \text{ }^\circ\text{C}$ for another 20 h. The FAS modified silica nanoparticles (FMS) were then collected by sedimentation, washed with ethanol to remove the residual FAS, and dried in vacuum at $50 \text{ }^\circ\text{C}$. The FMS were finally redispersed in butyl acetate for further use.

FAS modified silica nanoparticles were characterized by Fourier transform infrared spectroscopy (FT-IR) analysis, as shown in Fig. S1. A new peak at 1200 cm^{-1} assigned

to the C-F stretching vibrations and two absorption peaks at 2983 and 2916 cm^{-1} ascribed to antisymmetric and symmetric C-H stretching modes occurred. These results confirmed the successful bonding of FAS to the silica nanoparticles.

Fabrication of superhydrophobic coatings

Firstly, 4.5 g of PS, 1.9 g of PMSF and 40 g of butyl acetate were charged into a 250 mL plastic beaker and stirred at low speed to obtain the homogeneous solution. Then, FMS and TiO_2 nanoparticles were added to the beaker and stirred at a speed of 2000 r/min for 1h to get FMS/ TiO_2 -based nanocomposite coatings. TS-530/ TiO_2 -based nanocomposite coatings were prepared with the same procedure. The coatings were cast on aluminum substrates using a drawdown rod (120 μm) and dried at ambient temperature for one day 30 min to directly obtain superhydrophobic surfaces. The above procedure is schematically illustrated in Fig. S2.

Characterization

FT-IR measurements were carried out with a Nicolet Nexus 470 spectrometer (ThermoFisher, USA), in the wavenumber range of 400-4000 cm^{-1} , with a resolution of 0.5 cm^{-1} and an accumulation of 32 scans. The dried samples were blended with KBr to form sample plates. Water contact angle (WCA) and sliding angle (SA) were determined with an OCA15 contact angle analyzer (Dataphysics, Germany), using a 5 μL deionized water droplet. Average value from five parallel measurements was adopted. The artificial weatherability of superhydrophobic coatings were tested in a QUV accelerated weathering tester (QUV/se, Q-Panel Co., Ltd., USA), using UV lamps with a wavelength of 310 nm. The accelerated weathering cycle was set as follows: UV-irradiation at 60 $^{\circ}\text{C}$ for 4 h and irradiation intensity of 0.71 W m^{-2} , and condensation at 50 $^{\circ}\text{C}$ for 4 h. The surface morphology of the coatings was observed

using scanning electron microscopy (SEM Philips XL 30) at an accelerating voltage of 10 kV. The surface composition of coating 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 C1S at 284.6 eV. The topography of the coatings was observed using atomic force microscopy (AFM, Nanoscope IV system, Digital Instruments, Veeco, Plainview, NY) under a tapping mode and ambient conditions. The root-mean-square roughness (RMS) was calculated from the images using image analysis software. The morphology of the coatings was characterized using HIROX digital microscope KH-7700.

The abrasion resistance of the superhydrophobic surfaces was evaluated by a homemade polish tester, which comprises a piece of 1500-mesh sandpaper and two weights, 500 g and 1000 g. The sandpaper had a contact area of 2.25×2.25 cm² with the underlying superhydrophobic coating, and was dragged in one direction with a speed of 1 cm·s⁻¹. The resistance of coatings to oily contaminant was examined using oleic acid as the model pollutants. A thin layer of oleic acid was sprayed on the coating surfaces. Then, the coatings were put into the accelerated weathering tester. The WCAs were measured after 12 hours of time interval.

Outdoor exposure experiments were carried out at the Handan Road campus of Fudan University in Shanghai, China. The location was about 200 m away from any streets. All the coated panels were mounted on an outdoor exposure rack and exposed outdoors on a rooftop facing south with tilting angle of 45°. The exposure date spanned from April 22 to July 22, 2013. The changes of water contact angle (WCA) of the paints were periodically recorded.

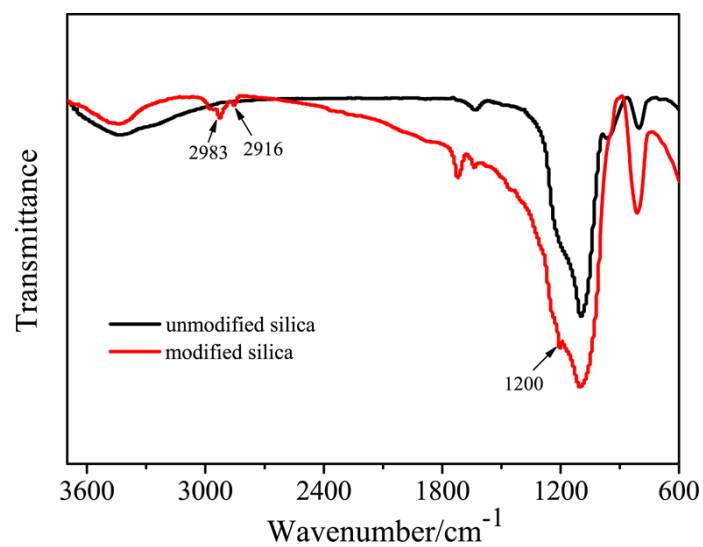


Fig. S1 FT-IR spectra of unmodified silica nanoparticles and FAS modified silica.

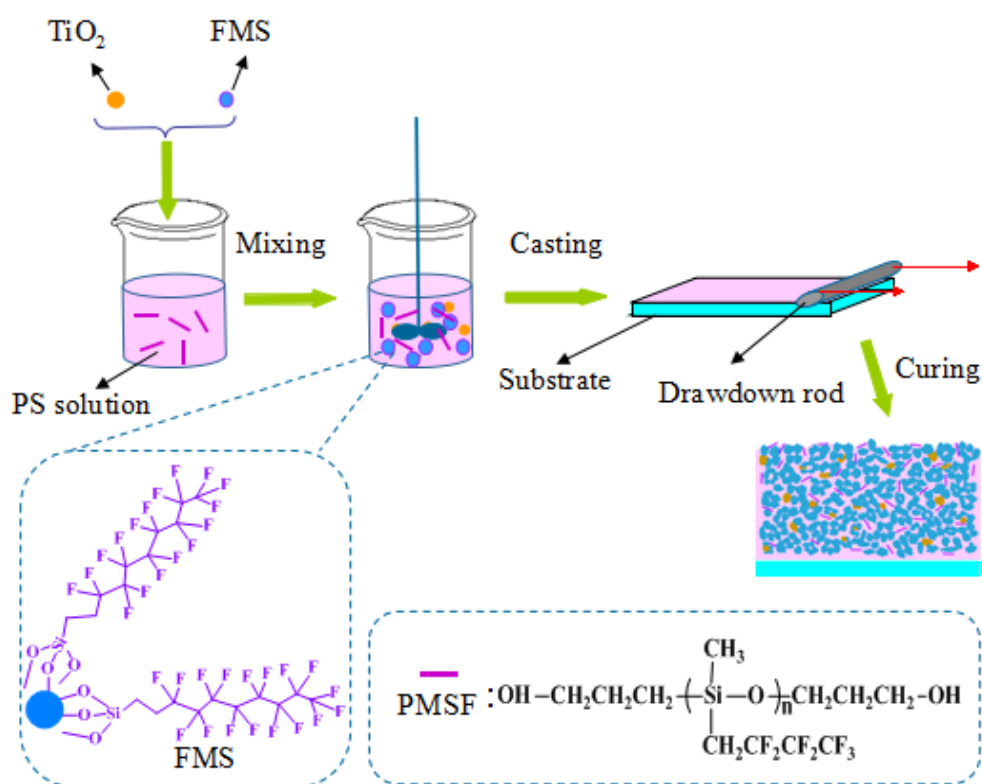


Fig. S2 Schematic illustration of the route to get self-repairing superhydrophobic coatings.

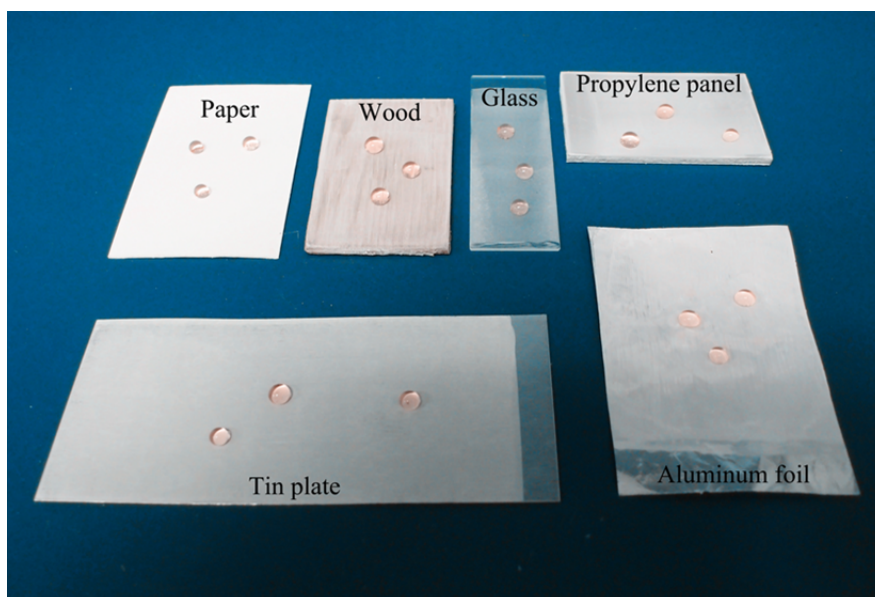


Fig. S3 The appearance of the FMS/TiO₂-based superhydrophobic coatings on different substrates: paper, wood panel, glass slide, propylene panel, tin plate and aluminum foil. (coating composition: PMSF/PS/FMS/P25= 17.1/40.9/36.0/6.0 wt/wt)

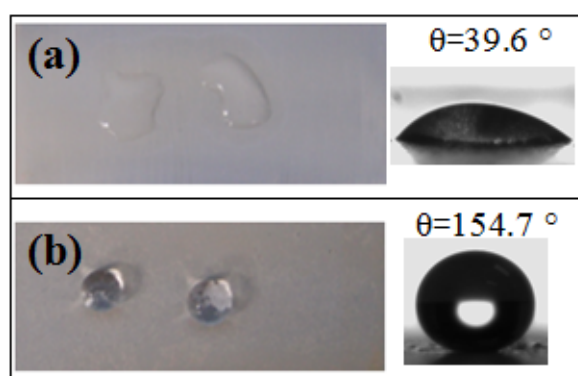


Fig. S4 Photograph images of water droplets and contact angles on TS-530/TiO₂-based (a) and FMS/TiO₂-based (b) superhydrophobic coating surfaces after UV-irradiated for 720 h in an accelerated weathering tester. (TS-530/TiO₂-based coating composition: PMSF/PS/TS-530/P25=20.4/48.6/25.0/6.0 wt/wt; FMS/TiO₂-based coating composition: PMSF/PS/FMS/P25=19.5/46.5/28.0/6.0 wt/wt).

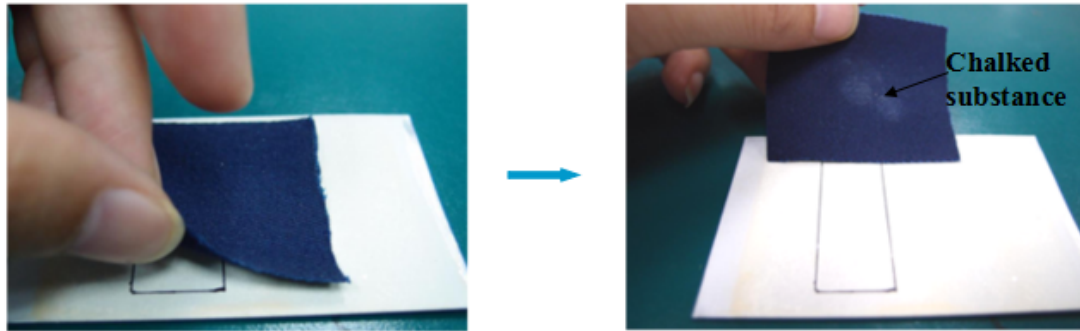


Fig. S5 Photographs of the chalked surface of FMS/TiO₂-based superhydrophobic coating after UV irradiation for 72 h. (coating composition: PMSF/PS/FMS/P25= 17.1/40.9/36.0/6.0 wt/wt)

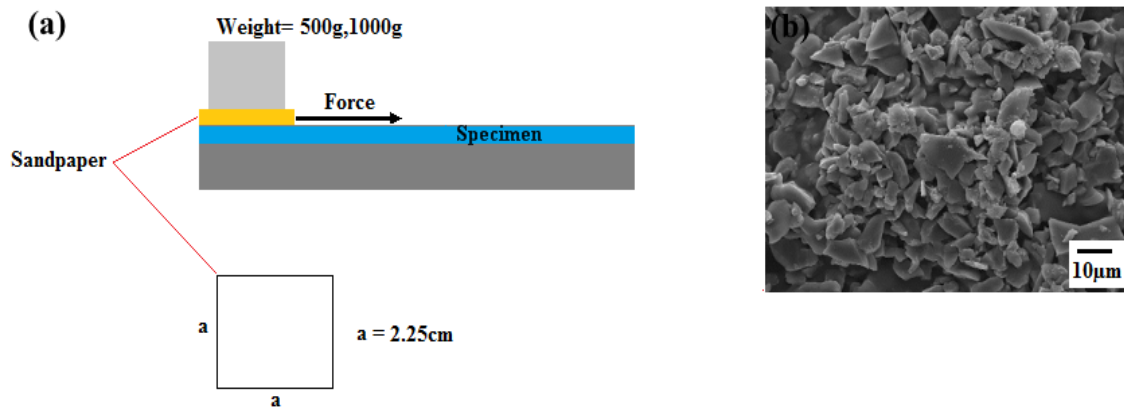


Fig. S6 (a) Schematic illustration of polishing experiment, (b) SEM image of sandpaper surface

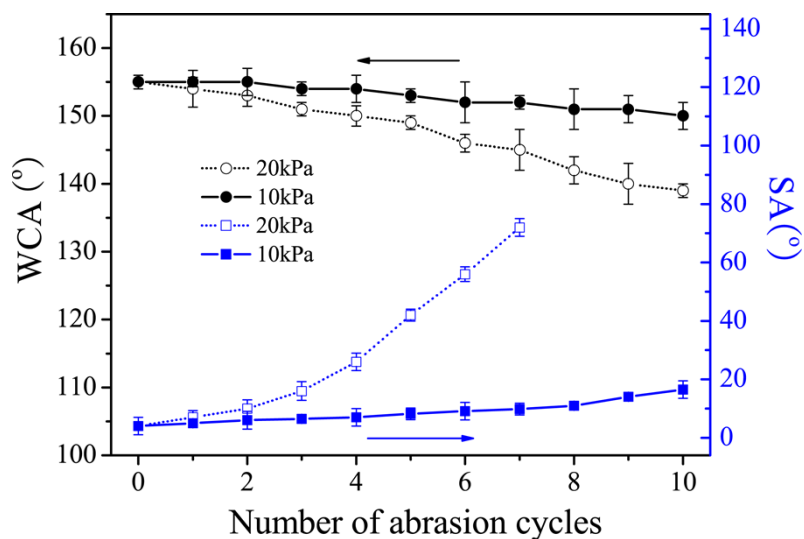


Fig. S7 The variation of WCA and SA with abrasion cycles for the FMS/TiO₂-based superhydrophobic coatings. (Coating composition: PMSF/PS/FMS/P25= 17.1/40.9/36.0/6.0 wt/wt)

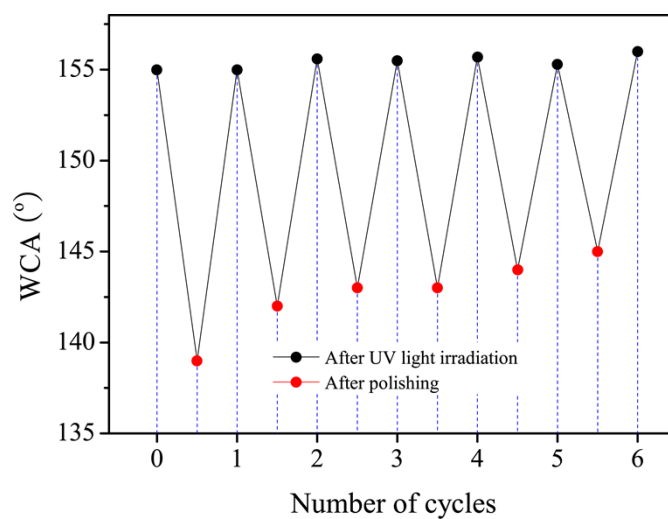


Fig. S8 Changes of WCA for the superhydrophobic coatings as a function of the repeated cycle number of the polishing under 20 kPa pressure and accelerated weathering. (Coating composition: PMSF/PS/FMS/P25= 17.1/40.9/36.0/6.0 wt/wt)

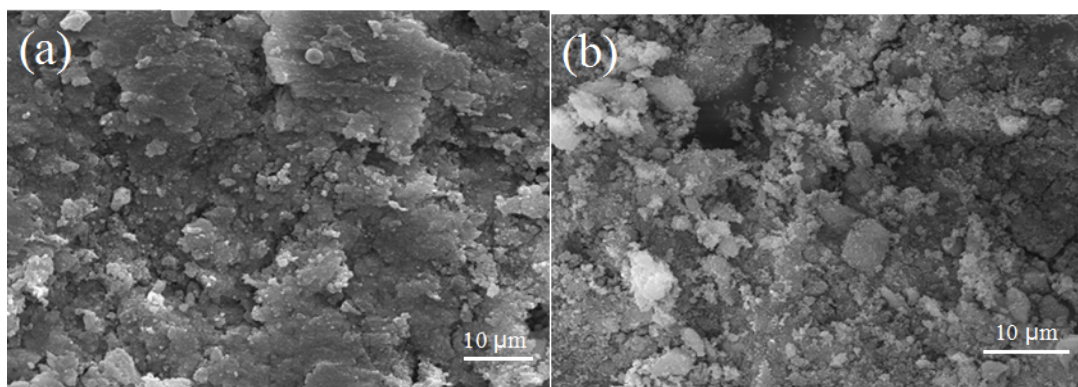


Fig. S9 (a, b) SEM images of the polished surface after 10 cycles of abrasion under a 10 kPa pressure (a), and the surface with 192 h accelerated weathering test (b). (Coating composition: PMSF/PS/FMS/P25= 17.1/40.9/36.0/6.0 wt/wt)

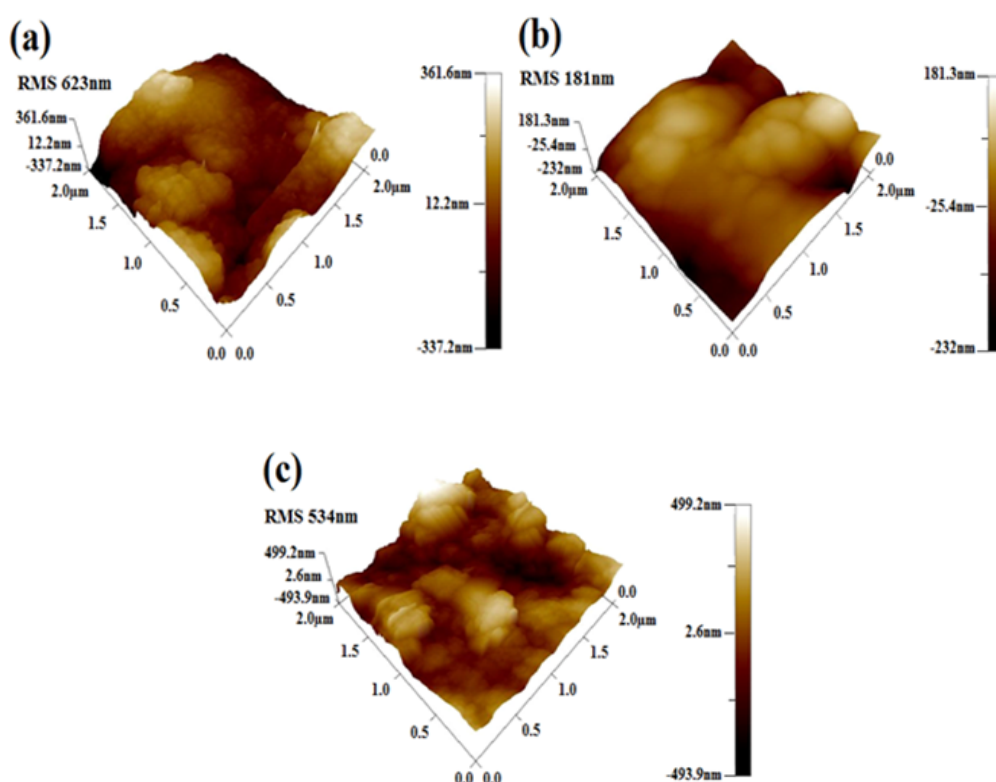


Fig. S10 AFM images of the FMS/TiO₂-based superhydrophobic coatings (a: original surface; b: the surface was polished for ten repeated cycles under 20 kPa pressure; c: the surface was polished for ten repeated cycles under 20kPa pressure and then UV-irradiated for 192 h in an accelerated weathering tester). (Coating composition: PMSF/PS/FMS/P25= 17.1/40.9/36.0/6.0 wt/wt)

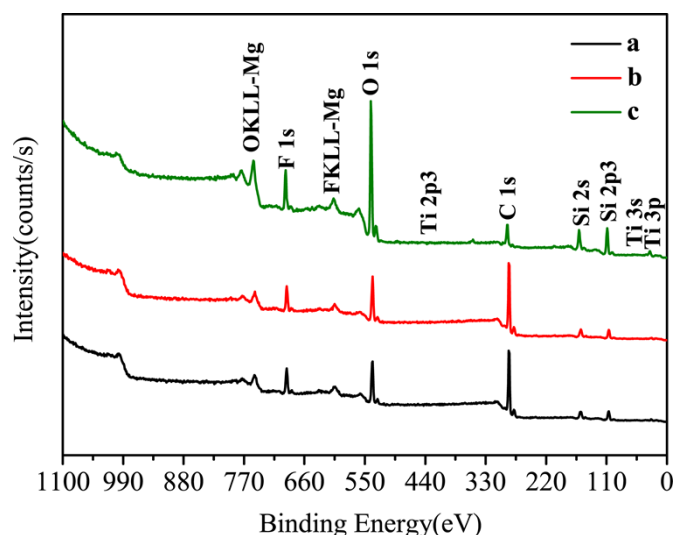


Fig. S11 XPS analysis of the surface of FMS/TiO₂-based superhydrophobic nanocomposite coatings (a: original surface; b: after ten cycles of abrasion under a 20kPa pressure; c: after 192 hours' accelerated weathering test). (PMSF/PS/FMS/P25= 17.1/40.9/36.0/6.0 wt/wt)

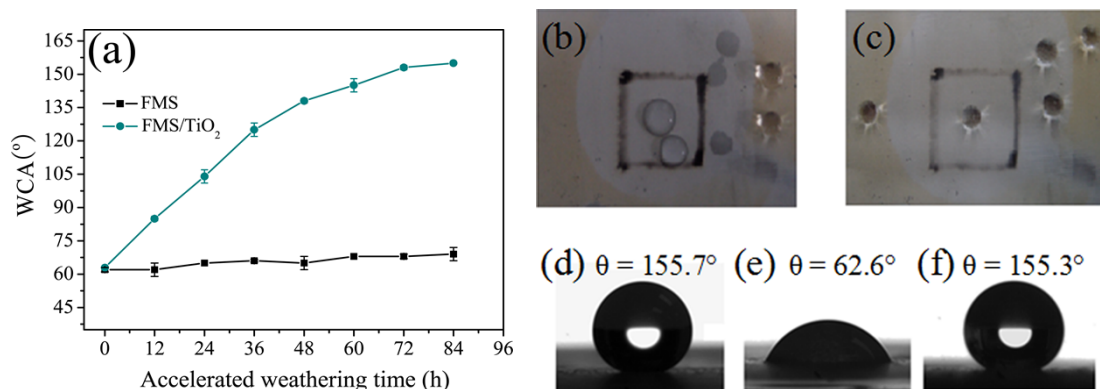


Fig. S12 (a) Changes of WCA for the FMS/TiO₂-based and FMS-based superhydrophobic coatings as a function of UV irradiation time, the surfaces were cast by a thin layer of oleic acid; (b-f) photographs of water droplets on a FMS/TiO₂-based superhydrophobic coating surface (b: after adhesion of oleic acid, c: after UV-irradiated for 84 h in an accelerated weathering tester) and contact angles on a FMS/TiO₂-based superhydrophobic coating surface before (d) and after the adhesion of oleic acid (e) and after UV-irradiated for 84 h in an accelerated weathering tester (f) (FMS-based superhydrophobic coating composition: PMSF/PS/FMS =17.7/42.3/40 wt/wt, FMS/TiO₂-based superhydrophobic coating composition: PMSF/PS/FMS/P25= 17.1/40.9/36.0/6.0 wt/wt);

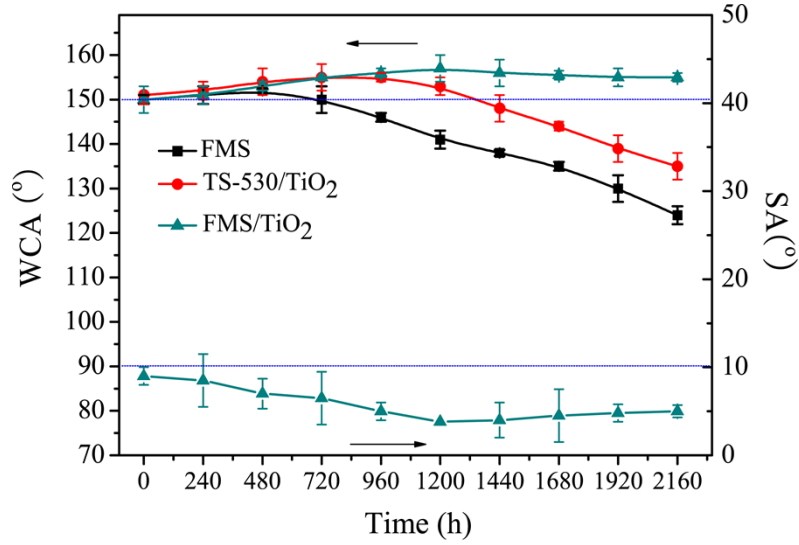


Fig. S13 Changes of WCA of FMS-based, TS-530/TiO₂-based and FMS/TiO₂-based superhydrophobic coatings during outdoor exposure (FMS-based superhydrophobic coating composition: PMSF/PS/FMS=20.1/47.9/32 wt/wt, TS-530/TiO₂-based superhydrophobic coating composition: PMSF/PS/TS-530/P25=20.4/48.6/25.0/6.0 wt/wt, FMS/TiO₂-based superhydrophobic coating composition: PMSF/PS/FMS/P25=19.5/46.5/28.0/6.0 wt/wt).