Supplementary Information

Robust super-hydrophobic coatings with micro- and nano-composite morphology

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Content：

Supplementary Experimental Methods:

Materials: Silicon dioxide (15nm, 40nm, 70nm, 200nm) were purchased from Aladdin Industrial Corporation (China), 3-Methacryloxypropyltrimethoxysilane (Dynasylan MEMO) was provided by Evonik Specialty Chemicals, while (Heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane (FAS) was offered by Diamondchem. Glass slide, ammonia water ($NH_3{\cdot}H_2O$) and C_2H_5OH were provided from Beijing Chemical Works.

Sample preparation: The modified solution was fabricated as described below: First, add 4g SiO_2 to 200g alcohol, stirring and ultrasound 10 min in 45℃, then append 3-Methacryloxypropyltrimethoxysilane, keep ultrasound 4h. Second, mixture 2g $NH_3{\cdot}H_2O$ and 10g H_2O, add to above-mentioned solution drop by drop, keep ultrasound 1h. Final, oil bath 18h (Referred to as the modified coating). The superhydrophobic coatings (SCs surface) were made as follows: Prior to the deposition of the hydrophobic coating on glass substrate. First, the substrate was cleaned by the plasma treatment, which led to the increased surface energy and water contact angle decreased, generating super-clean surface. Second, the substrate was immersed in the silane solution for approximately 16h, the silane solution was prepared under basic condition from the 3-Methacryloxypropyltrimethoxysilane, C_2H_5OH, $NH_3{\cdot}H_2O$ and H_2O in the molar ratio of 2:100:1:5 respectively (Referred to as 2% silane solution). Third, take out the glass, clean with alcohol, baking for ovens. We take the modified solution spray on the glass, baking then ultraviolet irradiation for 40 min. Last, we obtained SC by the method of fluorosilanization by CVD in FAS.

Surface characterization: The surface chemical composition of SC surface was analyzed with X-ray photoelectron spectroscopy (XPS), which gave the information about the various chemical bonds. The microstructure of SC surface was observed by field emission scanning electron microscopy (FESEM, JSM-7500F, JEOL, Japan) and atomic force microscope (AFM, Bruker Dimension Icon, USA). The roughness properties of SC surface, e.g., average roughness (Ra), root mean square roughness (RMS) were analyzed by analyst software of AFM. The wettability of SC was evaluated by measuring the contact angle of water droplet, which using the optical contact angle meter system (OCA40Micro, Dataphysics Instruments GmbH, Germany). The static water contact angles were measured at five different positions for each sample, and the average value was adopted as the contact angle. The sliding angle of the water droplet was observed by putting the water droplet on horizontal surface and then slowly tilting the surface until the droplet started sliding. The wetting behavior was recorded by high-speed camera (Phantom v9.1, Vision Research, USA) and charge coupled device camera (OCA40Micro, Dataphysics Instruments GmbH, Germany) with time scale at the ambient temperature. Time zero was chosen to be the frame in which deposited droplets contacted with the surface. The transmittance of SC was measured by ultraviolet-visible spectrophotometer (UV-Vis). The optical images were captured from the video obtained by Canon EOS 60D camera. UV aging experiments on the SC surface were equipped by UV curing lamp. The experimental wavelength was ranged in 320-450 nm. The analysis of the elements contain in SC surface after friction was measured by energy dispersive spectrometer (EDS) (INCA Energy 250, OXFORD INSTUMENTS). All the tests were repeated at least five times. The droplet volume was 5μL in contact angle (CA) measurement.

***Estimation of hysteresis*:** The adhesive force was assessed by a high-sensitivity micro-electromechanical balance system. We put the sample flat on the stage, and a 5μL water droplet was suspended on a metal ring. In this test, when the surface of the sample was in contact with the droplet, the balance force kept zero. The surface was moved at a speed of 0.02 mm s^{-1}. When the surface was in contact and detaches from the water droplet, the balance force gradually increased and reached the maximum. Finally, when the surface was completely disengaged from the droplet, the balance force drops immediately, completing a cycle of measurement. The value of tangent adhesive force was obtained by the analysis of Dataphysics system (DCA21, Dataphysics, Germany).

Test of hardness: The pencil was used to scratch the coating, for penetrating the coating to reach the substrate hardness test. According to ISO15184, the coating hardness chose zhonghua pencils, which adopted a set of hardness pencils of the range 6B-9H. The result indicated that hardness of the coating was 1H in this experiment.

Supplementary Figure Legends (Fig. S1-6):

Fig. S1:

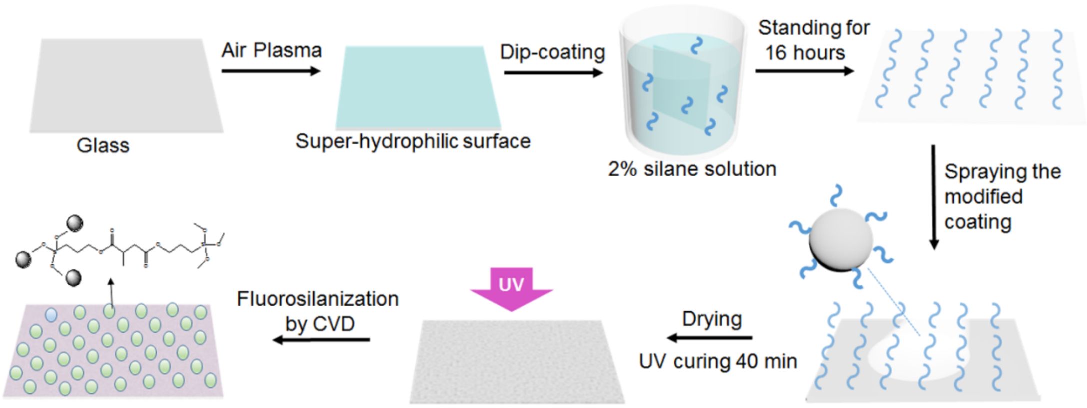

Fig. S1 Schematic illustration for the fabrication of superhydrophobic coating (SC) surface. The glass is treated by air plasma to prepare super-hydrophilic surfaces. The treated glass is soaked in 2% silane solution for 16 hours. After taking out the glass, and drying, the modified coating is sprayed over glass. After drying out, it is irradiated with ultraviolet light for 40 min to obtain good wear resistance. Finally, it is in fluorosilanization by CVD to get super-hydrophobicity, and the SC surface was prepared successfully.

Fig. S2:

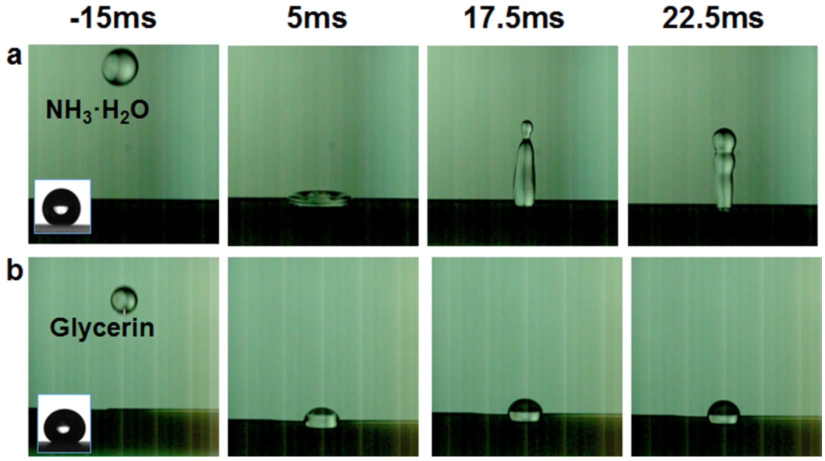

Fig. S2 a) Time-lapse photographs that $NH_3 \cdot H_2O$ droplet bounces on SC surfaces. The impact of $NH_3 \cdot H_2O$ achieves bouncing movement. Inset images show that contact angle of $NH_3 \cdot H_2O$ droplet is 151.3°. **b**) Time-lapse photographs that glycerol droplet stays on SC surface rather than bounces. The inset image indicates glycerol contact angle of 140.1°. It is mainly because of the surface tension of ammonia, glycerol and water are different, and the viscosity of glycerol is larger. So water, ammonia and glycerol have three different bounce phenomena. The droplet volumes are 5 μL.

Fig. S3:

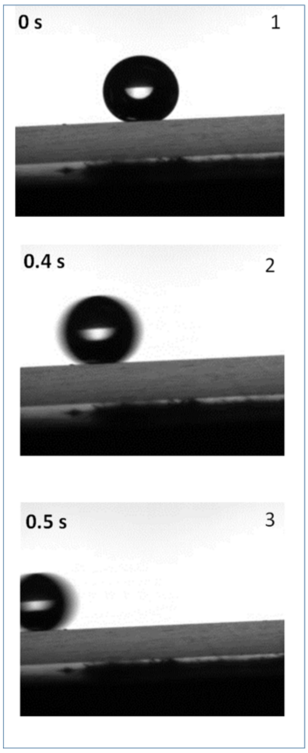

Fig. S3 Droplet sliding off SC surface. Water droplet cannot wet the surface and keep near-spherical shape. The surface adhesion is low to make the droplet easy to roll away. The water droplet cannot stay on the surface when the surface is inclined at a small angle (~ 4°), that is, the sliding angle is ~ 4°. Volume of water droplet is 5 μL.

Fig. S4:

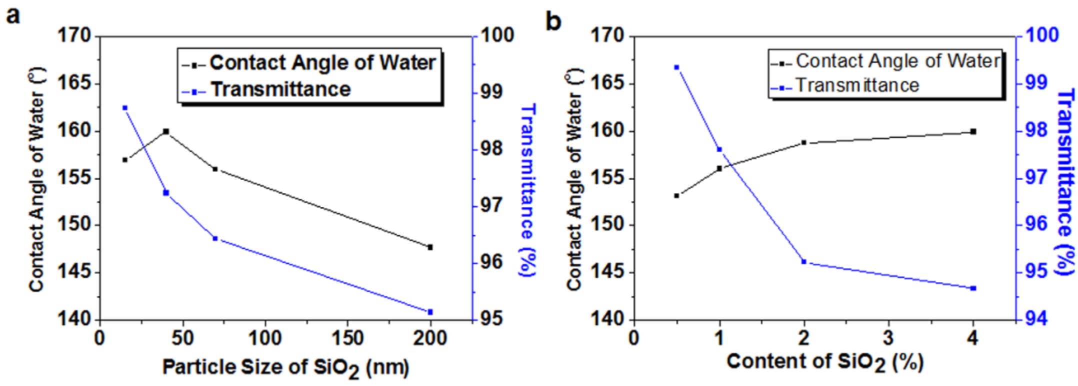

Fig. S4 a) Different particle sizes of silicon dioxide for the influence of CA and the light transmittance. The different particle sizes of silica, including gas-phase nano-silica at 15 nm, 40 nm, 70nm and 200nm, respectively. When the silica particle size is relatively small, the particles are small and the degree of dispersion is uniform, resulting in a higher degree of transparency. With the increase in particle size, light transmission significantly decreases. When the silica particle size is 200 nm, the contact angle lowered due to the large adhesion, and the transparency of the coating remarkably reduced. Therefore, we chose to test the optimum test conditions at a particle size of 40 nm. **b)** Influence of silicon dioxide content for CA and transparency. The silica with a diameter of 40 nm, with the silica content of 0.5%, 1%, 2% and 4% is observed for changes of its contact angle and light transmittance. When the silica content of silicon dioxide is different, its contact angle and light transmittance are changing. With the increase in the content of silica, the contact angle of the coating will be correspondingly larger, at the same time, the light transmittance will be reduced. According to the information of the diagram, considering the relative optimization of contact angle and light transmittance, we chose the best experimental conditions for the content of 2% of the silica under the experiment.

Fig. S5:

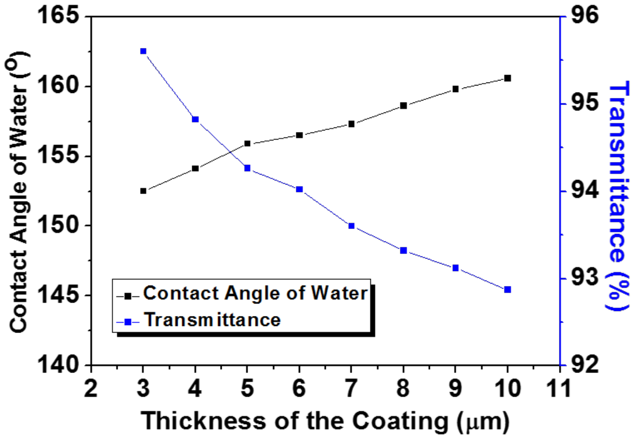

Fig. S5 The relationship between contact angle and light transmittance in different thicknesses. Different thicknesses (3-10 μm) of the coating produce different light transmission effects (ranged in 92.8-95.6%). The thicker thickness of the coating induced the weaker light transmission, and the greater contact angle.

Fig. S6:

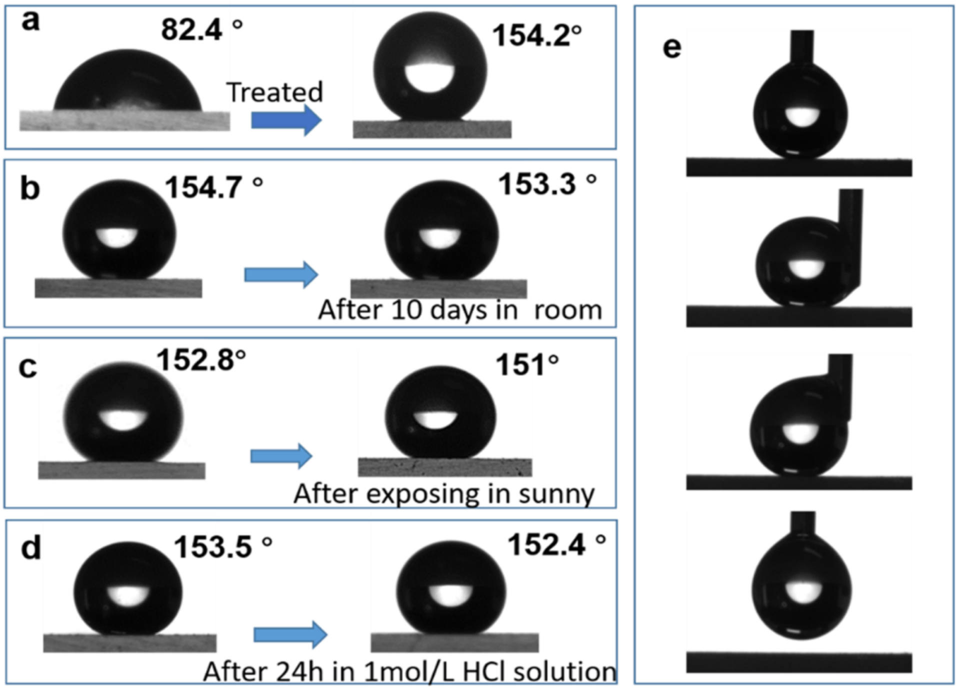

Fig. S6 a) Water contact angle changes before fluorination and after fluorination. We have prepared the superhydrophobic coating by fluorosilanization by CVD and the contact angle after fluoride can be increased from 82.4 ° to 154.2 °. **b)** Water contact angle changes before and after 10 days at room temperature. The SC surface has a long period of stability at room temperature. The contact angle hardly changes after natural placement at room temperature for almost 10 days, and the hydrophobicity is well maintained. **c)** Water contact angle on SC surface is still reach 150° when exposed to a high temperature of 35℃ outside for four hours. **d)** Water contact angle changes after 24h in 1 moL/L HCl solution. We immerse the SC surface in 1 moL/L HCl solution for 24 hours and measure the contact angle before and after the experiment. The contact angle has no obvious change, and the superhydrophobic state was maintained. **e)** The movement of droplets on SC surface after high temperature of 35℃ outside for four hours, the droplets can remain spherical on SC surface and can be free to move without wetting the SC surface. The droplet volumes are 5 μL.

Supplementary Movies:

Movie S1: The water droplet bounces up on SC surface.

Movie S2: The Brine droplet bounces up on SC surface.

Movie S3: The droplet (CH_2Cl_2:H_2O in the molar ratio of 1:20) bounces up on SC surface.

Movie S4: The droplet (CH_2O_2:H_2O in the molar ratio of 1:20) bounces up on SC surface.

Movie S5: The $NH_3 \cdot H_2O$ droplet slightly bounces up on SC surface.

Movie S6: The glycerol droplet doesn’t bounce up on SC surface.

Movie S7: The droplet sliding off the slope SC surface.

Movie S8: The water droplets sweep away the dirt contaminants completely on SC surface.

Movie S9: The water droplets sweep away the oil contaminants completely on SC surface.