

## *Supplementary Information*

### **Facile preparation of superhydrophobic coating by spraying a fluorinated acrylic random copolymer micelle solution**

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#### **Experimental section**

##### **Materials**

Dodecafluoroheptyl methacrylate (DFMA) was supplied by Harbin Xeogia fluorine-silicon chemical Co., Ltd., China. Butyl acrylate (BA), methyl methacrylate (MMA), and 2-hydroxyethyl methacrylate (HEMA) were purchased from Kemiou Chemical Co., Tianjin, China. All the monomers were purified by washing with 5 wt% NaOH aqueous solution and water, respectively, and dried with MgSO<sub>4</sub> and distilled under vacuum. Methyl isobutyl ketone (MIBK), ethyl acetate (EA), and azobisisobutyronitrile (AIBN) were also purchased from Kemiou Chemical Co., Tianjin, China. Other chemicals were used as received without further purification.

##### **Synthesis of the fluorinated acrylic copolymer (FAC)**

The fluorinated acrylic random copolymer containing 20 wt% DFMA was prepared by radical solution polymerization. The polymerization was carried out under nitrogen atmosphere in a 250-mL four-neck flask equipped with reflux condenser, mechanical stirrer, dropping funnel and a nitrogen inlet. After MMA, BA and HEMA (6/4.5/1, wt/wt/wt) were polymerized using AIBN as an initiator in MIBK at 75°C for 1.5 h, the monomer DFMA together with MIBK and AIBN were added drop-by-drop within 1 h. Afterward the reaction mixture was stirred for another 3 h at 80 °C. The reaction was stopped by cooling to room temperature. The resultant polymer was precipitated in hexane, filtered, and then dried under vacuum at 40°C for 24 h.

##### **Preparation of the superhydrophobic fluorinated acrylic copolymer (SFAC) coating**

A certain amount of the prepared fluorinated acrylic random copolymer was dissolved in a mixture of EA and MIBK with different volume ratios of 10/0, 9/1, 7/3, 5/5 and 3/7, respectively to form 10 wt% solutions. The superhydrophobic coatings were obtained by spraying the copolymer solution over substrates uniformly under a certain air pressure (0.8MPa), and then dried at room temperature. During the spraying process, the nozzle of spray gun with diameter of approximately 0.8~2 mm was kept at a certain distances (5cm and 15cm) from the substrate and the polymer solution was atomized to large numbers of tiny liquid droplets with the average diameter of ~17 μm at the spray gun nozzle. The room temperature and relative humidity were ~25±5°C and 50±10%, respectively.

### Preparation of hydrophobic fluorinated acrylic copolymer (HFAC) coating

The HFAC films were prepared by spin-coating of the copolymer/MIBK solution on the substrate at room temperature. The spinning speed was set at 300 rpm (6 s) and 2000 rpm (10 s) for the first and second steps, respectively. The room temperature and relative humidity were  $\sim 25 \pm 5^\circ\text{C}$  and  $50 \pm 10\%$ , respectively.

### Characterizations

FT-IR spectra of samples were recorded between  $4000\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$  in an AVATER-360B spectrophotometer using KBr pellet technique. The FT-IR spectrum of FAC is shown in Fig. S1. The molar mass distribution was determined in a Waters 515-2414 gel permeation chromatography (GPC) with THF as the eluent flowing at 1 mL/min. Polystyrene standards were used to generate a calibration curve.

The diluted copolymer solution was deposited onto a copper net and stained with phosphotungstic acid solution and then freeze-dried. TEM micrographs were taken with JEOL JEM100CXII transmission electron microscope.

The surface morphology of the SFAC coatings was observed with a scanning electron microscope (SEM, FEL Nova Nano 430).

The surface composition of coating was measured by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ECSA) using at a  $90^\circ$  take-off angle.

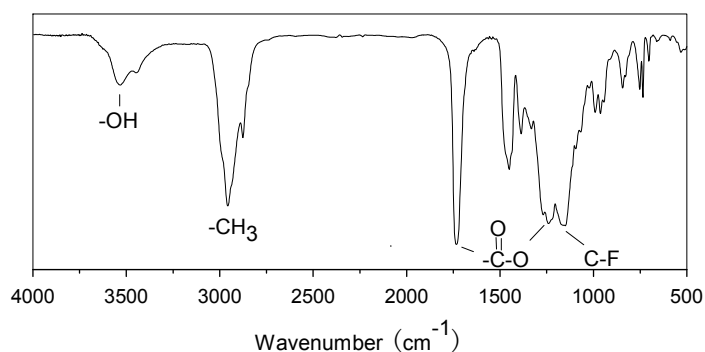
Water contact angles and sliding angles on the surfaces at different temperatures were measured with a modified optical contact angle meter system with cold plate (JC2000D, Shanghai Zhongchen Equipment Ltd., China). The cold plate could control the temperature of the sample surface to range from  $-30^\circ\text{C}$  to  $60^\circ\text{C}$  with a precision of  $0.2^\circ\text{C}$ . The measurements were carried out with  $4\ \mu\text{L}$  water droplets under nitrogen (relative humidity  $< 10\%$ ).

The modified optical contact angle meter system with a high speed CCD camera (Fig. S3) was also utilized to observe the profiles of individual water droplets on sample substrates at  $-20^\circ\text{C}$  in a freezing process. The freezing process of water droplets was recorded by the high speed CCD camera at a speed of 25f/s. the sample substrates were maintained at  $-20^\circ\text{C}$  under nitrogen (relative humidity  $< 10\%$ ).

The heat changes during the freezing process of water droplets on sample plates at  $-20^\circ\text{C}$  were measured by a modified differential scanning calorimeter (DSC, Perkin-Elmer Pyris Diamond DSC) (Fig. 6a). The distance between the tip of needle and the substrate is 2 cm, and needle gauge control the droplet size. The thickness of the sample coatings are  $40 \pm 1.5\ \mu\text{m}$ .

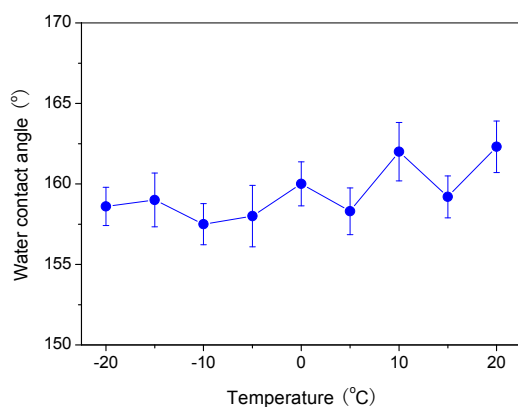
The anti-icing measurement of SFAC coatings: The formation of ice on SFAC coatings were determined by putting them in an oven with a temperature of  $-20^\circ\text{C}$ . The coated and uncoated Al plates are tilted at an angle of about  $15^\circ$  during the experiments. A volume of 600mL of supercooled water ( $-20^\circ\text{C}$ ) is poured onto the plates in about 10 s at approximately constant rate from a bottle located about 5 cm above. The amount of ice was qualitatively examined with naked eyes.

## Results

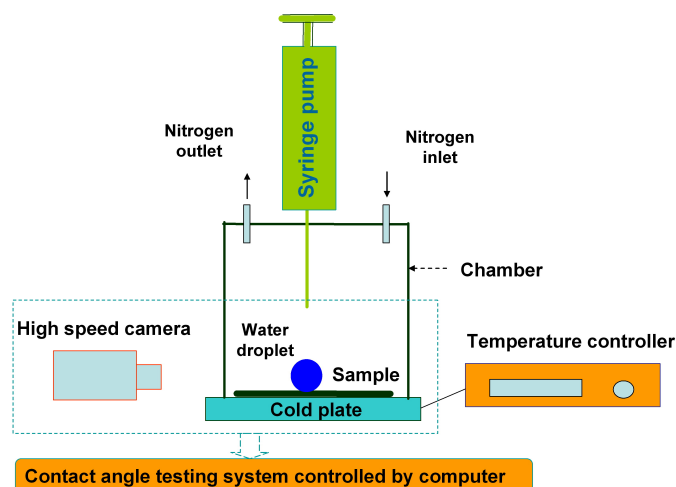


**Fig. S1** FT-IR spectrum of FAC.

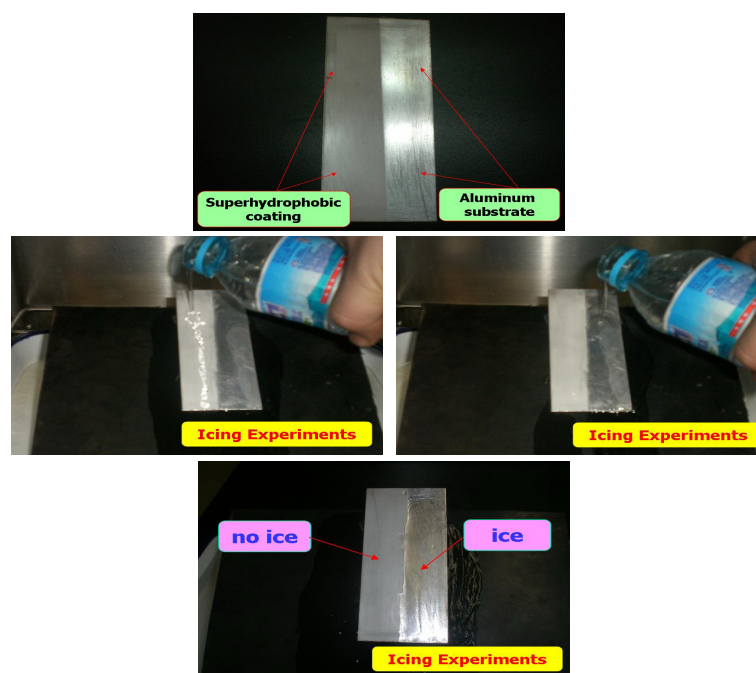
Fig. S1 shows the FT-IR spectra of FAC. The characteristic stretching peaks of C-OH, C-H and C=O group were obviously shown at 3500 cm<sup>-1</sup>, 2850~3000 cm<sup>-1</sup> and 1735 cm<sup>-1</sup>, respectively resulting from copolymer containing -CH<sub>2</sub>- and -CH<sub>3</sub> and C=O groups. The peak at 1248 cm<sup>-1</sup> was the characteristic bonds of C-O in  $\text{—}\overset{\text{O}}{\parallel}\text{C—}$  of the copolymer. In addition, the bands at 1145 cm<sup>-1</sup> and 675 cm<sup>-1</sup> were attributed to stretching and bending vibrations of C-F. The peak at 1640 cm<sup>-1</sup>, which was attributed to the stretching vibration of C=C group, disappeared, indicating that the monomers were polymerized.



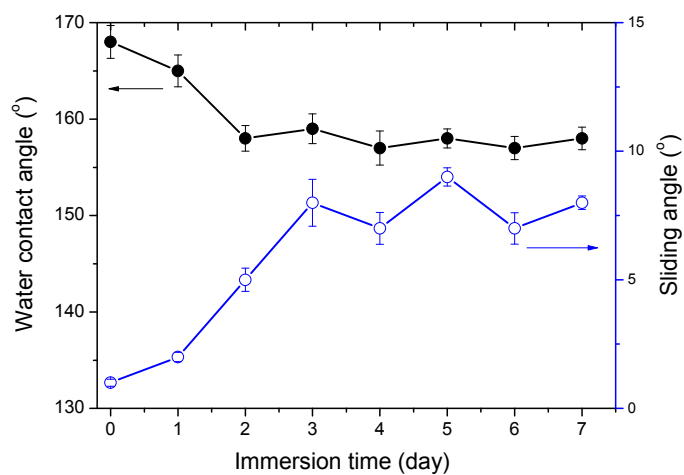
**Fig. S2** Effect of the measuring temperature on water contact angles of the SFAC coating under N<sub>2</sub>.



**Fig. S3** Schematic drawing of the modified contact angle testing system.

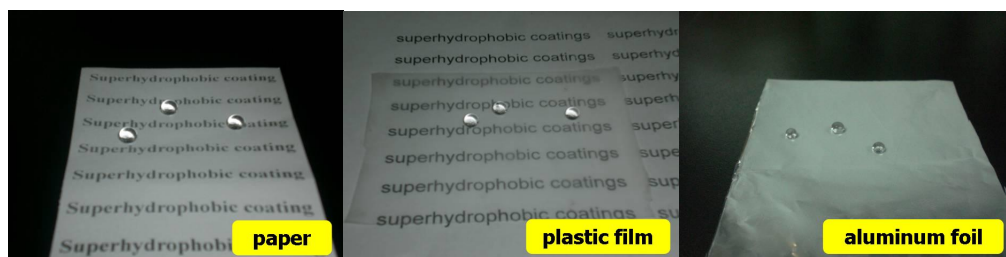


**Fig. S4** Typical digital photographs taken during the icing experiment of SFAC coating and aluminum at  $-20^{\circ}\text{C}$ .



**Fig. S5** Water contact and sliding angles on the SFAC coating as function of the immersion time in deionized water.

The SFAC coating durability in water was studied by the following method. The coating sample is soaked in water for a certain time. After a definite time of immersion, the sample is removed from the water, dried with an ash-free filter, and then measured for values of water contact and sliding angles (Fig. S8). Although the contact angle has slight decline and the sliding angle has a little ascent, SFAC coating can maintain its superhydrophobic character ( $\text{WCA} > 150^{\circ}$ ,  $\text{SA} < 10^{\circ}$ ) after being immersed in water for 7 days, displaying excellent long-term durability in water.



**Fig. S6** Photographs of water droplets (10  $\mu$ L) on the spray-coated paper, plastic film, and aluminum foil.