Supporting Information

Two-Dimensional MXene-Reinforced Robust Surface Superhydrophobicity with Self-Cleaning and Photothermal-Actuating Binary Effects

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1. Experimental Section

Synthesis of multilayered $Ti_3C_2T_x$ MXene. The multilayered MXene (m-$Ti_3C_2T_x$) was synthesized as follows: [1,2] 1 g of Ti_3AlC_2 MAX powders were immersed in 10 ml of a 50 wt% concentrated HF solution (purchased from Sinopharm Chemical Reagent Co., Ltd.) for 18 h with continuously magnetic stirring at room temperature (RT) to remove Al layer. The obtained suspension was washed with deionized water for several times until the pH of the supernatant reached to about 6. The final sediment (m-$Ti_3C_2T_x$) was collected and then dried for 24 h in vacuum oven at 60 ^oC.

Synthesis of delaminated $Ti_3C_2T_x$ MXene. To obtain the delaminated MXene (m-$Ti_3C_2T_x$) flakes, 25 wt% Tetrapropylammonium hydroxide (TPAOH, purchased from J&K Scientific Co., Ltd., Beijing, China) aqueous solution was used for intercalation process. [3] In this case, the m-$Ti_3C_2T_x$ powders were dispersed in TPAOH solution, at a ratio of 1 g m-$Ti_3C_2T_x$ of TPAOH per 10 ml, respectively, for 3 d at RT under magnetic stirring. Then, the suspension was washed with ethanol and deionized water for three times to remove the residual TPAOH. Finally, the d-$Ti_3C_2T_x$ flakes were collected by freeze drying the black water suspension for further utilization.

Preparation of superhydrophobic MXene coating. 400 mg of fluorinated alkyl silane (FAS, $C_8F_{13}H_4Si(OCH_2CH_3)_3$, purchased from Shanghai qinba chemical co., Ltd.) was placed into 35 ml of absolute ethanol, and subsequently the solution was stirred for 1 h at RT. Then, different amount of m-$Ti_3C_2T_x$ and d-$Ti_3C_2T_x$ were added into the above-mentioned solution and stirred for 3 h. After reaction, the FAS modified m-$Ti_3C_2T_x$ and d-$Ti_3C_2T_x$ powders were obtained under high-speed centrifugation with

12,000 r/min for 10 min. The initial weight ratios of m-$Ti_3C_2T_x$ to d-$Ti_3C_2T_x$ chosen were 1:2, 1:1and 2:1 and the resulting modified MXenes were denoted as m/d-F_1, m/d-F_2 and m/d-F_3, respectively. In all instances, the weight of the d-$Ti_3C_2T_x$ was 200 mg. The collected modified MXene powders, 150 mg polydimethylsiloxane (PDMS) and 15 mg curing agent were added to 10 ml of ethyl acetate solution (Sinopharm Chemical Reagent Co., Ltd.) and keep stirring for 30 min to get a uniform mixture. Finally, the mixture was sprayed or dripped onto various soft and hard substrates (such as filter paper, glass slide and cotton) and then cured at 120 ^oC for 2 h to obtain a superhydrophobic surface.

Fabrication of photothermal actuator. The actuators were fabricated using the superhydrophobic PDMS@m/d-F_2 coating with 200 mg d-$Ti_3C_2T_x$. Typically, PDMS@m/d-F_2 coating was dripped onto both sides of filter paper using a dropping pipette to ensure the uniform dispersion of superhydrophobic coating. After that, filter paper was designed for symmetric triangle shape or/and asymmetric structure to realize light-actuating behaviors under continuous irradiation of NIR laser (808 nm, 1W/cm^2). Meanwhile, the different kinds of photothermal actuating behaviors (e.g., directional linear motions or rotational motion) of the coated filter paper was manipulated by adjusting the irradiation position.

Characterization. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) were obtained using a high-resolution field-emission SEM (Hitachi S-4800, Japan). Transmission electron microscopy (TEM) images were obtained using a JEM-2100F transmission electron microscope. X-ray

diffraction (XRD) measurement was performed on an X-ray diffractometer (Rigaku D/max 2550 V). Atomic force microscope (AFM, Asylum Research) was used to investigate the surface roughness of the sample surfaces. Fourier transform infrared (FTIR) spectra were obtained on a FTIR spectrometer (FTIR-7600, Lambda Scientific, Australia). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi (Thermo Scientific, UK). Water contact angle (CA) measurements were performed on a CA measurement system (OCA 20 Dataphysics instruments GmbH, Germany) at ambient temperature with a 3 μL water droplet as the indicator. A 808 nm high-power multimode pump laser (Shanghai Connect Fiber Optics Co.) was used as the NIR light source with a spot radius of about 5 mm. An infrared thermal imaging instrument (FLIR A325SC camera) was used to detect the temperature and record the thermal image of the samples.

Durability measurements of the superhydrophobic surfaces. The mechanical durability tests (such as knife scratch, kneading, abrasion and cross-cut tape tests) were carried out on the coated filter papers, which glued to the glass slide surface. In the abrasion test, the coated paper weighting 200 g was placed face-down on sandpaper (grit no. 800), longitudinally and transversely moved for 10 cm along the ruler, respectively. This process is denoted as one abrasion cycle. The cross-cut tape test was implemented by using the double-sided adhesive tape to attach and detach from the coating surfaces. The chemical durability tests were conducted by measuring the CA of the coated glass slides after immersing them in hydrochloric acid (pH = 1) or sodium hydroxide (pH = 14) solution for different times. Filter paper coated with modified

MXene coating was exposed to NIR radiation (808 nm, power intensity = 1.0 W/cm^2) for different times to test the influence of NIR laser on the hydrophobic property of coating. Additionally, to investigate if the repeated cycles of NIR radiation affect the superhydrophobicity of the modified MXene coating, 808 nm NIR laser (power intensity = 1.0 W/cm^2) was used to irradiate the MXene coating for 5 min as one illumination cycle.

Photothermal performance of the MXene coating. To quantify the samples and reduce the error, modified MXene with various initial m-$Ti_3C_2T_x$ to d-$Ti_3C_2T_x$ weight ratio together with 75 mg PDMS and 7.5 mg curing agent were dispersed in ethyl acetate solution and further filtered onto the filter paper to investigate the photothermal performance. The weight ratios of m-$Ti_3C_2T_x$ to d-$Ti_3C_2T_x$ were set identical with preceding preparation ratio except for the 100 mg d-$Ti_3C_2T_x$. The photothermal performance of the samples were studied under 808 nm NIR laser with different power densities (0.25, 0.50, 0.75, 1.00, 1.25 W/cm^2). The photothermal conversion efficiency (η) of the modified MXene coating is determined according to the following equation: [4]

$$\eta = \frac{hA\Delta T_{max}}{I} \qquad (1)$$

Where h represents the heat transfer coefficient, A represents the surface area of the system, ΔT_{max} represents the temperature difference between the maximum temperature of the sample and ambient temperature, I represents the light power. In order to obtain the value of hA, t and θ, which denoted as the time and the ratio of ΔT to ΔT_{max}, respectively, were introduced to establish a functional relationship:

$$t = -\frac{\sum_i m_i c_{p,i}}{hA} ln\theta \quad (2)$$

Where m is the weight of coating, c_p is the specific heat of MXene, which could be determined using a method of sapphire with DSC instrument. Therefore, hA can be acquired by calculating the aforementioned linear equation from the cooling period. Substituting this value of hA into equation (1), the photothermal conversion efficiency (η) of MXene coating could be calculated.

The NIR laser induced pressure in the coated sample can be determined as follow: [5]

$$F = \frac{E}{ct} = \frac{P}{c} \quad (3)$$

Where F is the light induced pressure, E is the light energy, c is the velocity of light, t is time, P is the power of NIR laser.

2. Supplementary Figure

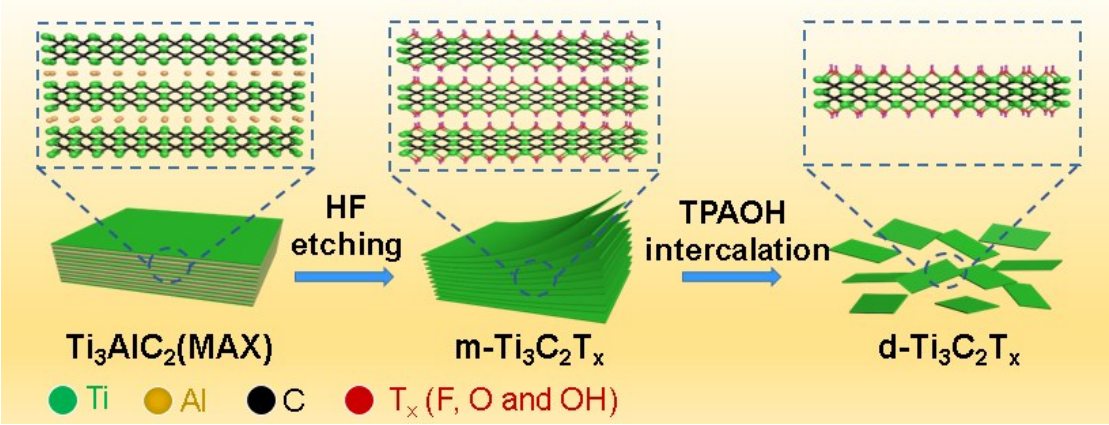

Fig. S1 Schematic diagram for the fabrication of m-$Ti_3C_2T_x$ and d-$Ti_3C_2T_x$, including HF etching and TPAOH intercalation.

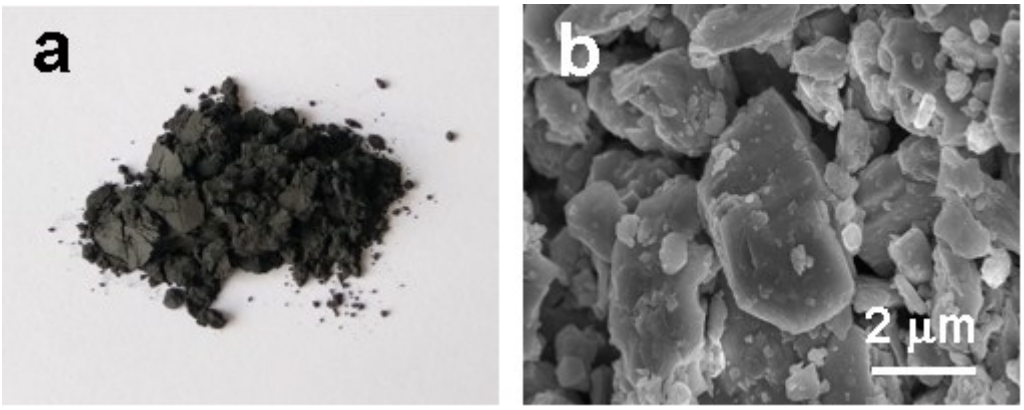

Fig. S2 (a) Digital photograph, and (b) SEM image of Ti_3AlC_2 (MAX phase).

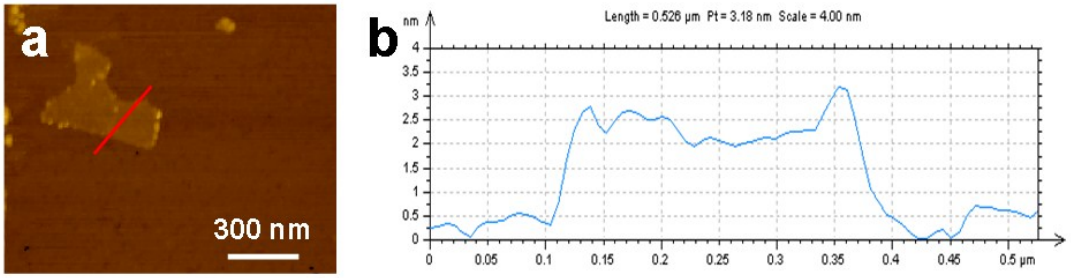

Fig. S3 (a) AFM image of d-$Ti_3C_2T_x$ nanosheet. (b) AFM-measured thickness of d-$Ti_3C_2T_x$ nanosheet.

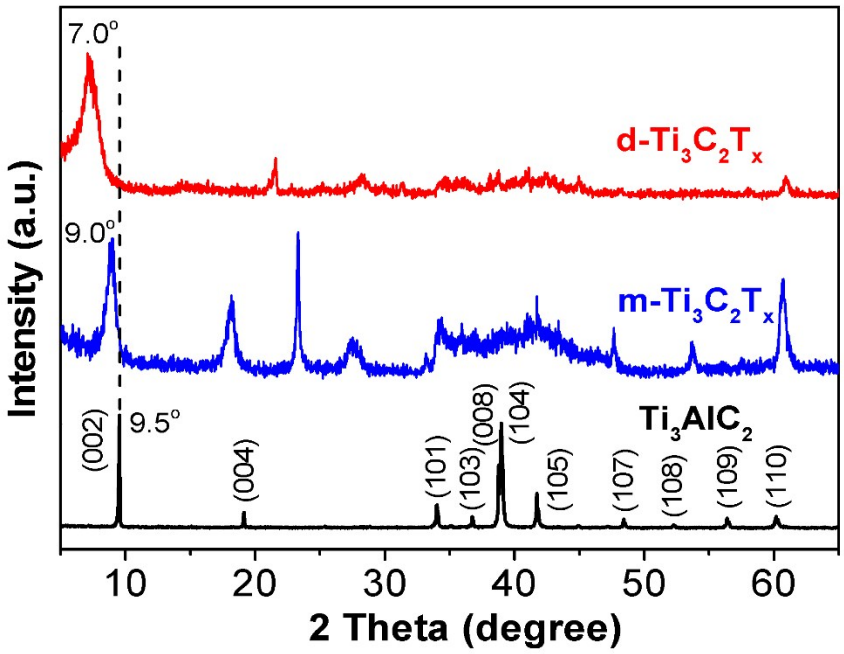

Fig. S4 XRD patterns of Ti_3AlC_2, m-$Ti_3C_2T_x$, and d-$Ti_3C_2T_x$. The distinct shift of (002) peak towards lower angles verifying the successful preparation of m-$Ti_3C_2T_x$ and d-$Ti_3C_2T_x$.

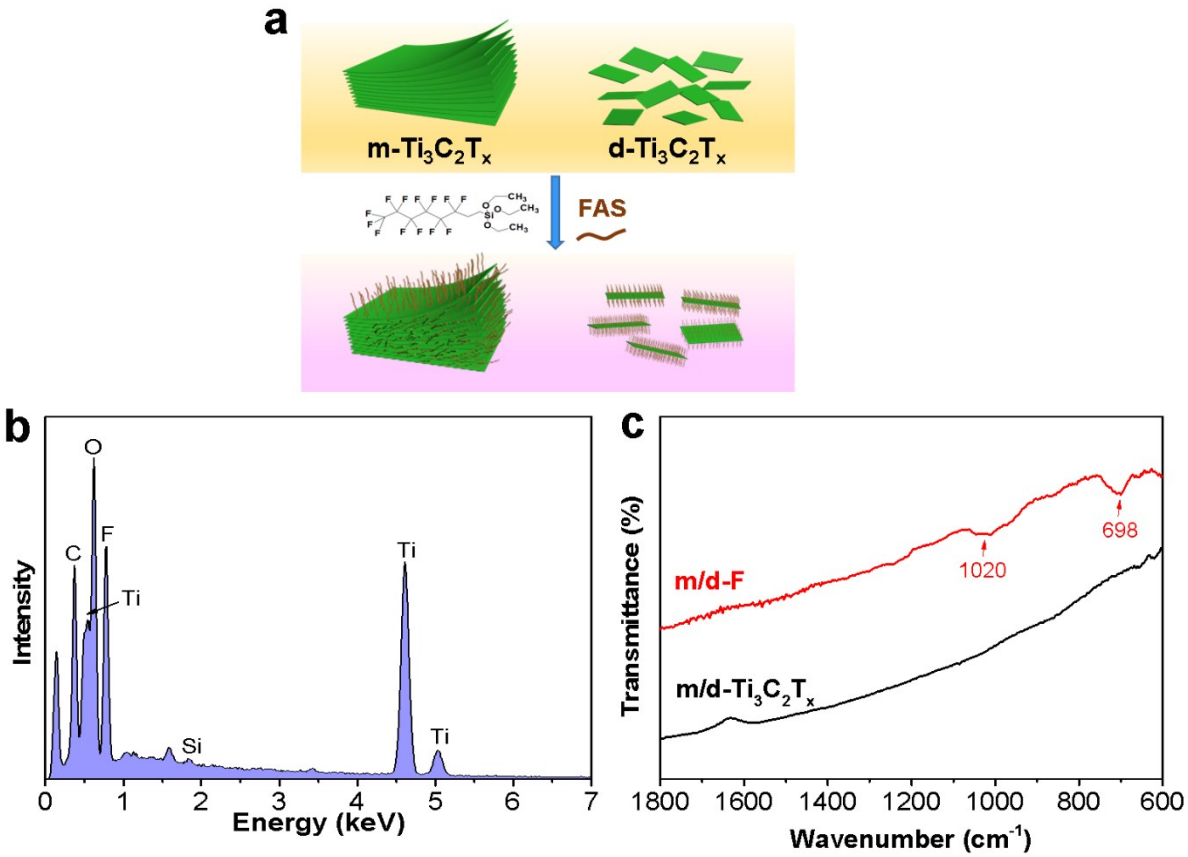

Fig. S5 (a) Schematics of surface modification of m-$Ti_3C_2T_x$ and d-$Ti_3C_2T_x$ using FAS.

(b) EDS spectra of m/d-F. (c) FTIR spectra of m/d-$Ti_3C_2T_x$ and m/d-F.

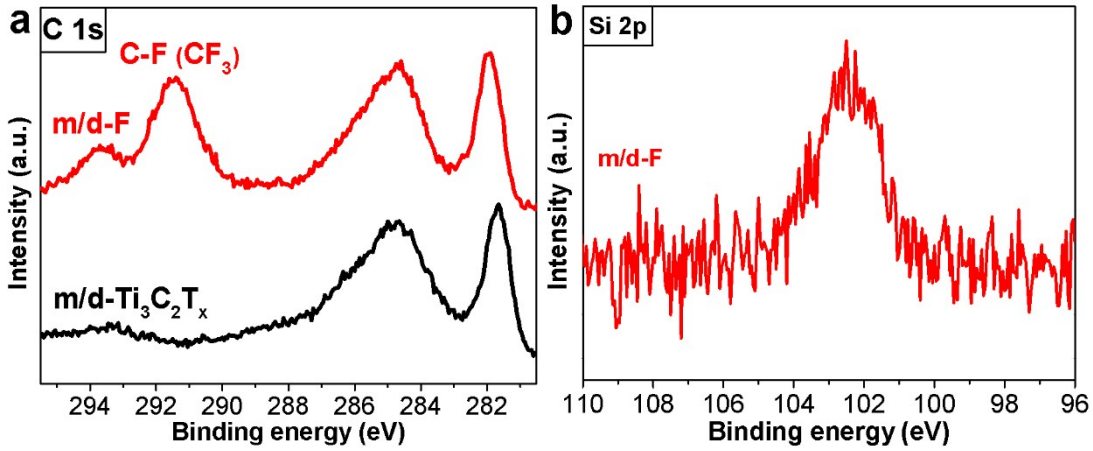

Fig. S6 (a) C 1s spectra of m/d-$Ti_3C_2T_x$ and m/d-F. (b) Si 2p spectum of m/d-F.

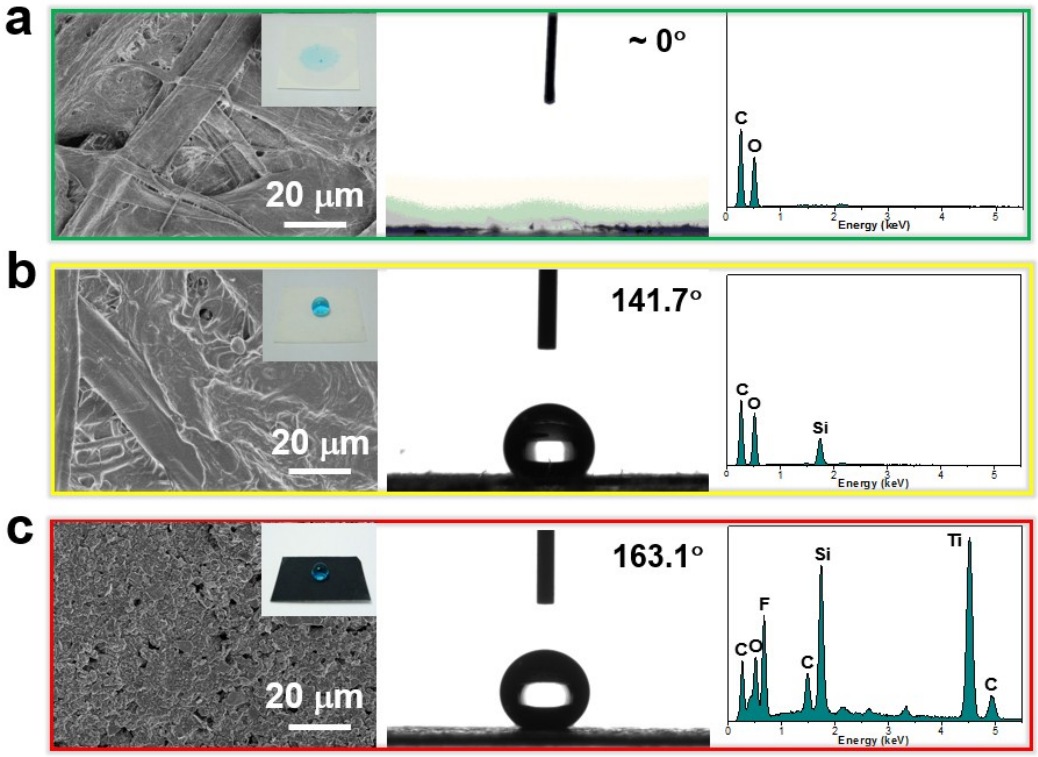

Fig. S7 SEM images, CA, and EDS measurements of different samples: (a) bare filter paper; (b) filter paper with PDMS; (c) filter paper with PDMS@m/d-F coating (initial weight ratios: m-$Ti_3C_2T_x$/d-$Ti_3C_2T_x$ = 1:1). Insert: water droplets on the surface of different filter samples.

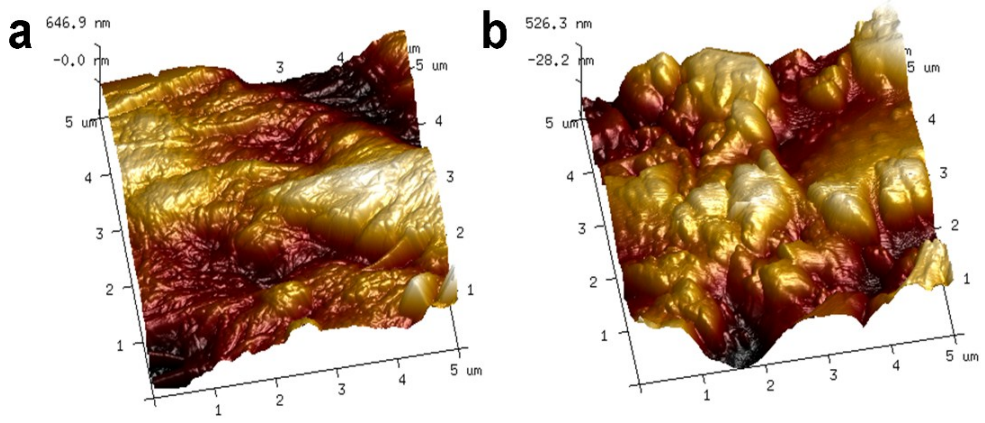

Fig. S8 AFM images of (a) bare filter paper, and (b) filter paper coated with PDMS@m/d-F (initial weight ratios: m-$Ti_3C_2T_x$/d-$Ti_3C_2T_x$ = 1:1).

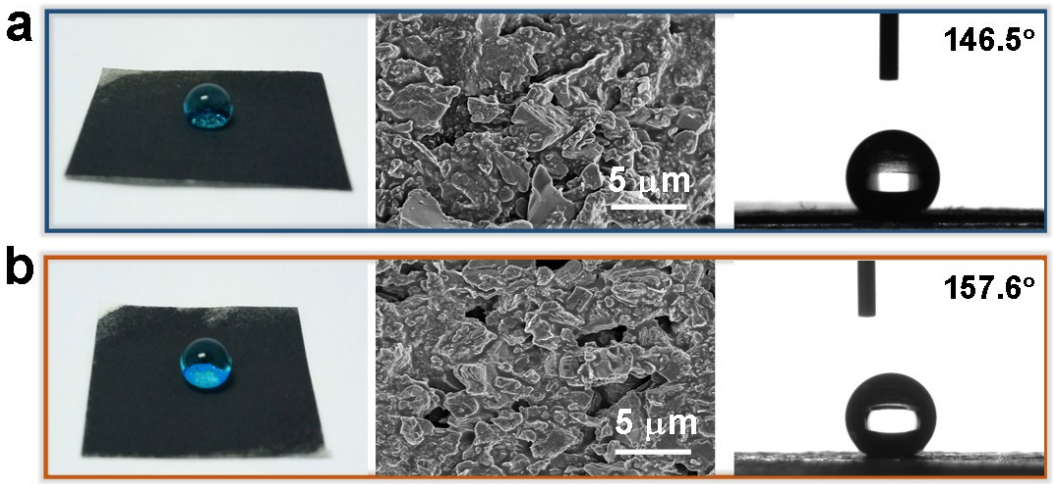

Fig. S9 Optical photographs, SEM images, and CA measurements of (a) PDMS@m/d-F_1, and (b) PDMS@m/d-F_3 coated on filter paper.

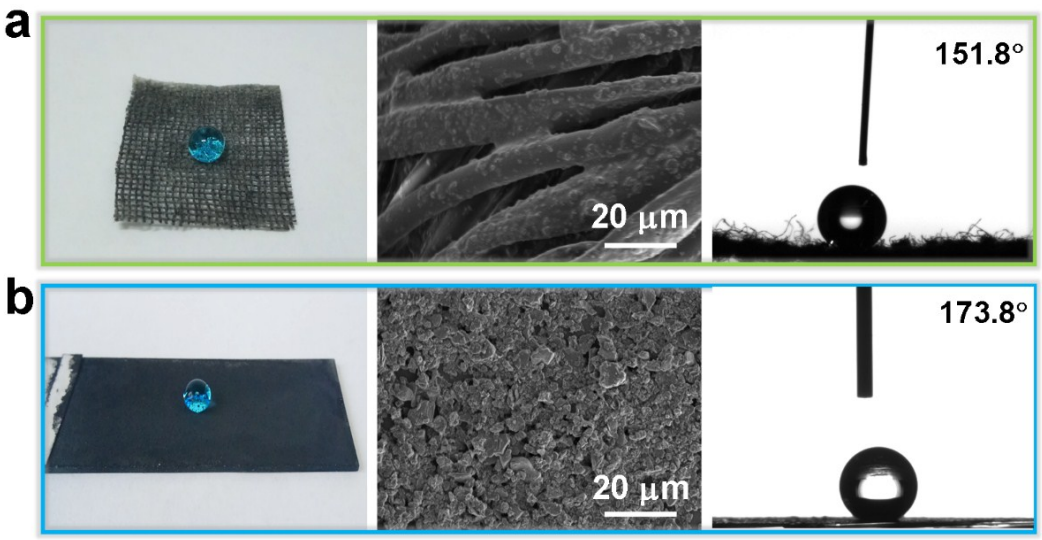

Fig. S10 Optical photographs, SEM images, and CA measurements of (a) cotton coated with PDMS@m/d-F_2, and (b) glass slide coated with PDMS@m/d-F_2.

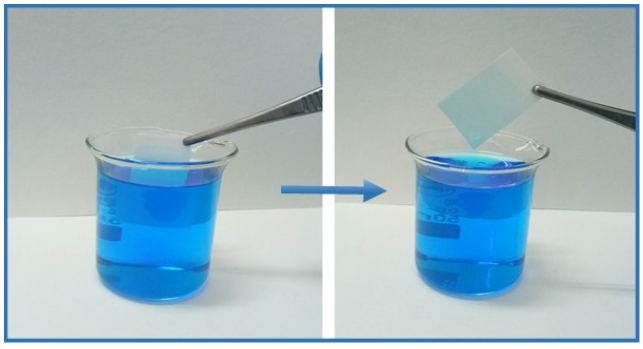

Fig. S11 Optical photographs showing the procedure of dipping an untreated filter paper into methylene blue staining water.

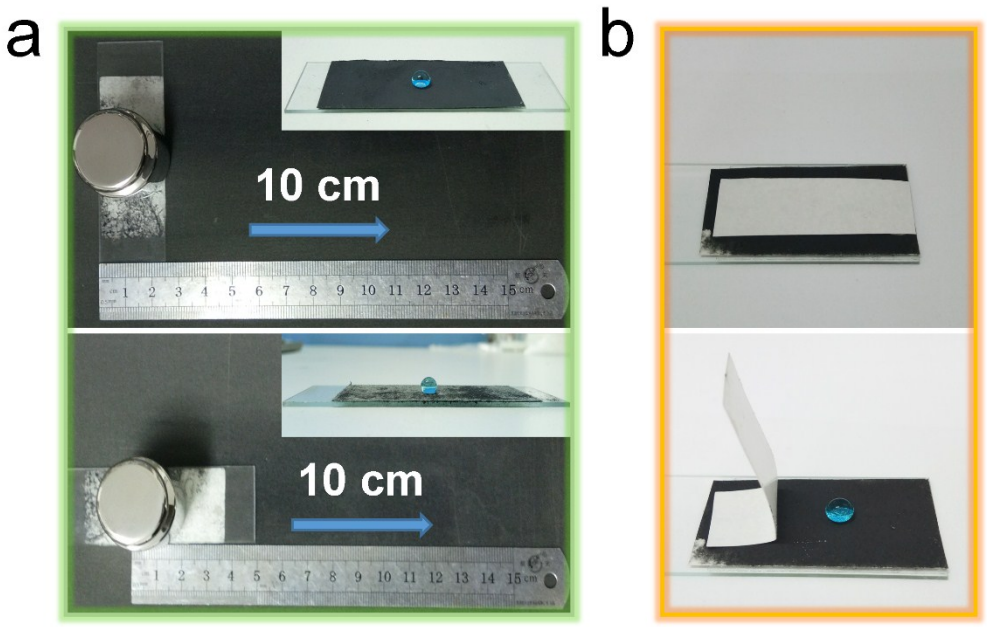

Fig. S12 (a) Sandpaper abrasion test of the coater filter paper, which glued to a glass surface. Insert: water drop on the coated filter paper surface before and after 10 abrasion cycles. (b) Photographs of the surface before (top) and after (bottom) the cross-cut tape test. A water droplet was placed on the pressed surface.

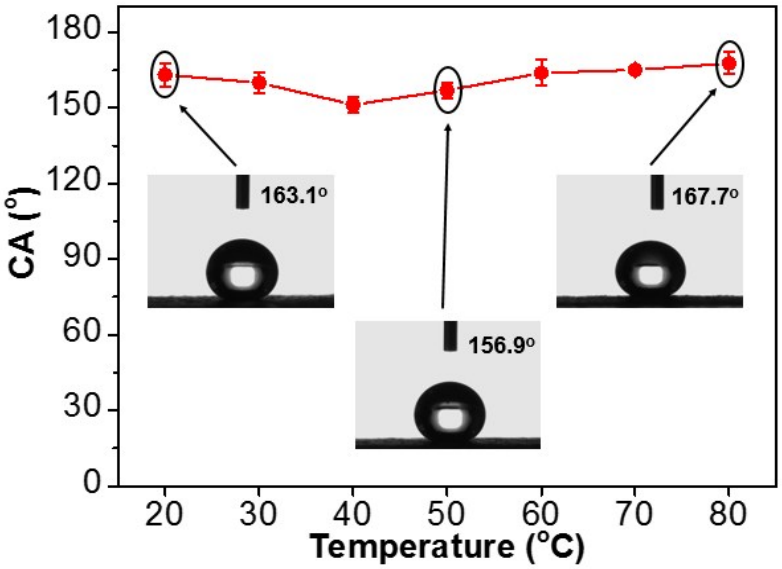

Fig. S13 Water CA of coated filter paper as a function of temperature. Images of 3 μL water droplet on the coating surface at 20, 50, and 80 °C were inserted.

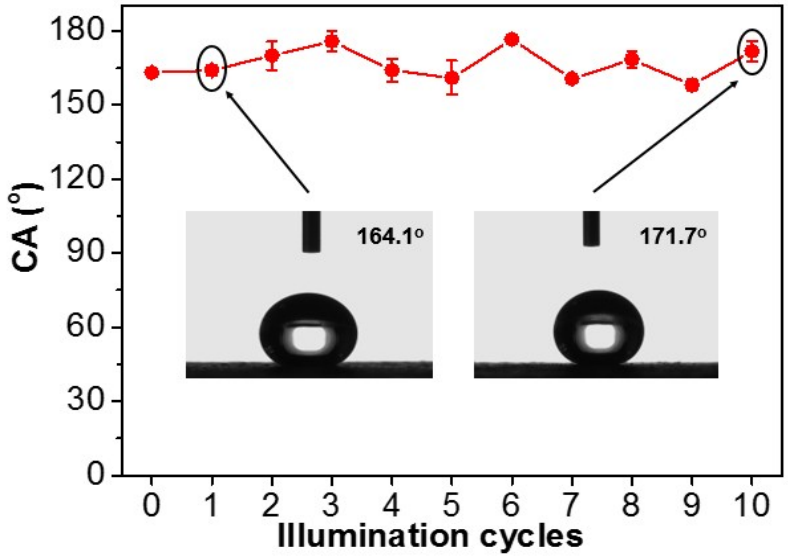

Fig. S14 Water CA of coated filter paper as a function of the number of NIR illumination cycles. Images of 3 μL water droplet on the coating surface after 1 and 10 illumination cycles.

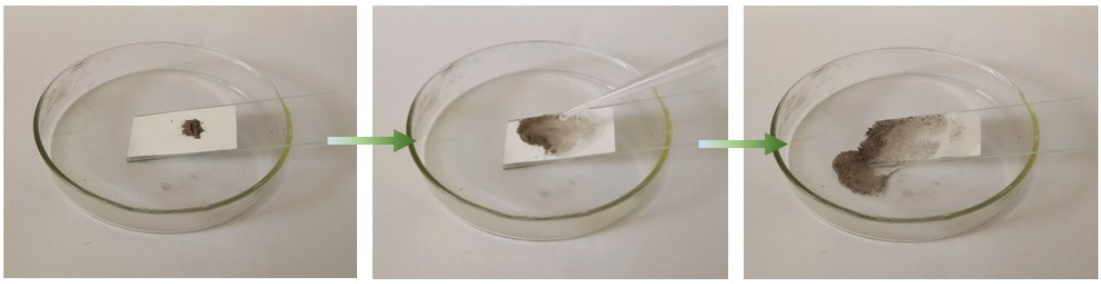

Fig. S15 Optical photographs showing the procedure of self-cleaning test on uncoated filter paper.

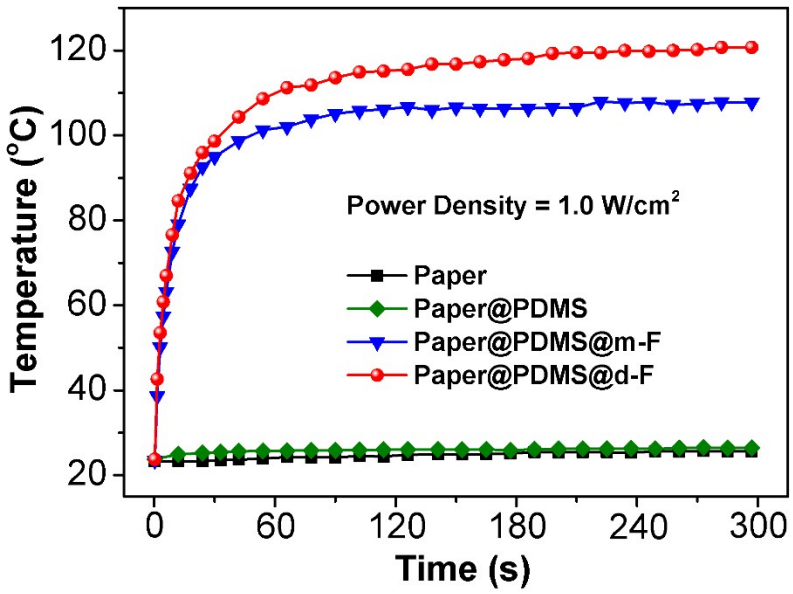

Fig. S16 Photothermal heating curves of various samples under 808 nm NIR light irradiation.

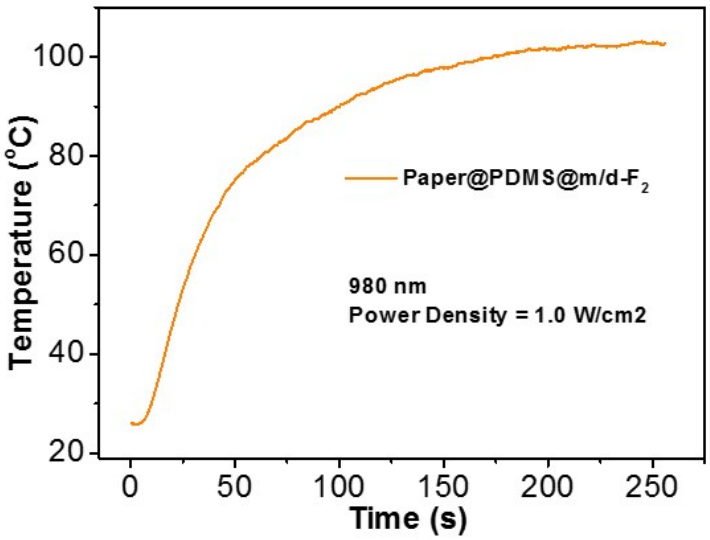

Fig. S17 Photothermal heating curves of PDMS@m/d-F_2 coating under 980 nm light irradiation.

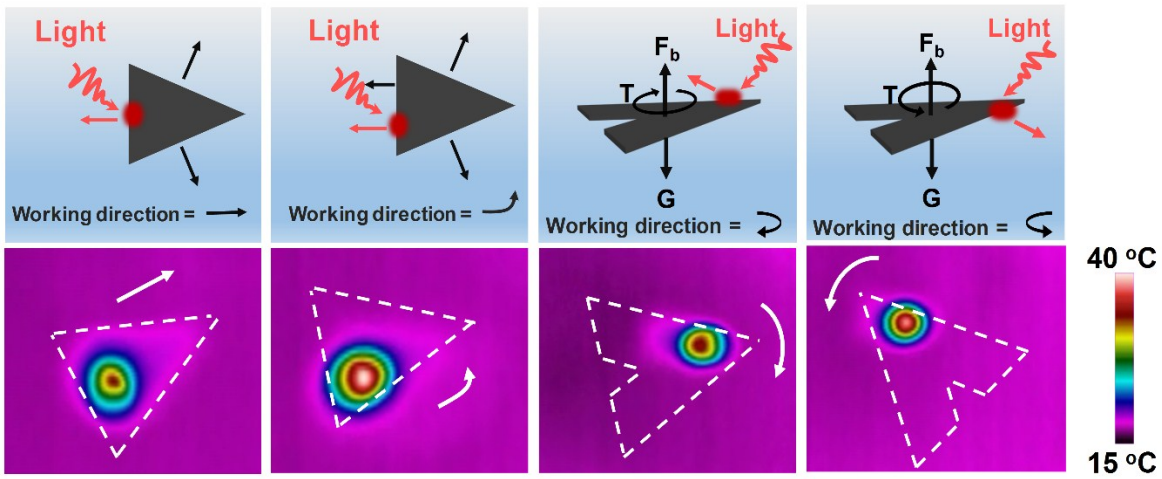

Fig. S18 The force analyses and thermography images of the coated filter paper for linear motions and rotational motions.

Supplementary Movie S1

This Movie shows the outstanding self-cleaning ability and behavior of the PDMS@m/d-F_2 coating.

Supplementary Movie S2

This Movie shows the remarkable liquid repellency of the PDMS@m/d-F_2 coating.

Supplementary Movie S3

This Movie shows the filter paper coated with PDMS@m/d-F_2 could obtain directional linear motions (e.g., forward propulsion or left/right turning propulsion) under the NIR laser irradiation.

Supplementary Movie S4

This Movie shows the coated filter paper could swerve in two opposite directions (i.e., clockwise, and anticlockwise rotational rotations) through a rational combination of the asymmetric structure and varied irradiation position.

Supplementary Information Reference:

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4. Y. Cao, J.-H. Dou, N.-j. Zhao, S. Zhang, Y.-Q. Zheng, J.-P. Zhang, J.-Y. Wang, J. Pei and Y. Wang, *Chem. Mater.*, 2016, **29**, 718-725.
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