Supporting Information to:

Self-healable and transparent PDMS-g-poly(fluorinated acrylate) coating with ultra-low ice adhesion strength for anti-icing application

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Experimental

1. Materials

Vinyl pendant polydimethylsiloxanes (V-PDMS) (Mn = 22000), 4-vinyl pyridine (vp), 2-Ethylhexyl acrylate (EHA)，3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Heptadecafluorodecyl methacrylate (TEMAc-8)，(3-Mercaptopropyl) Triethpxysilane (MTS), Cobalt chloride ,Benzoyl peroxide, KH570, Tetrahydrofuran were purchased from Aladdin (China). Meanwhile, 1,6-Hexaneadiamine (HD) was purchased from KESHI (China), whereas epoxy resin (EP) was provided by Hangzhou Wuhuigang Adhesive Co., Ltd (China). Hydrogen fluoride ether was provided by Quzhou Dongye Chemical Technology Co. Ltd (China). Silicone oil (SO) (Mn = 800) was purchased from Guangzhou Gongying Chemical Co. Ltd (China). All chemicals were used as purchased.

2. Preparation of PDMS-g-PFA-DB

Silicone elastomers grafted with pyridine groups (PDMS-g-PFA-DB) was initially prepared using the following procedure: V-PDMS (0.95 g), vp (0.53 wt%), EHA (5.26 wt%), TEMAc-8 (1.79 mmol), (3-Mercaptopropyl) triethpxysilane (3.16 wt%), Benzoyl peroxide (3.16 wt%) were mixed in hydrogen fluoride ether and the solution was stirred for 8 h at 70°. After that, the solution was left to stand for 5 hours to obtain a clear reaction solution, which was precipitated 3 times with methanol and finally dried under vacuum at 45° to obtain a translucent solid. The solid was dissolved in hydrogen fluoride ether. 0.03 wt% of cobalt chloride was added to the solution, and stirred at room temperature for 2 h. It was then poured onto a mold and cured at 90° for 20 minutes and then placed at 130° for 3 h to obtain PDMS-g-PFA-DB.

The preparation process of PDMS-g-PFA is similar to that of PDMS-g-PFA-DB, except that cobalt chloride is not added.

3. Preparation of PDMS-g-PFA-CB

Conventional chemically cross-linked PDMS-g-poly(fluorinated acrylate) (PDMS-g-PFA-CB) was prepared as follows: V-PDMS (0.95 g), EHA (5.26 wt%), TEMAc-8 (1.79 mmol), (3-Mercaptopropyl) triethpxysilane (4.21 wt%), KH 570 (5.26 wt%), Benzoyl peroxide (3.16 wt%) were mixed in hydrogen fluoride ether and the solution was stirred for 8 h at 70°. After that, the solution was left to stand for 5 hours to obtain a clear reaction solution, which was precipitated 3 times with methanol and

finally dried under vacuum at 45° to obtain a translucent solid. It was cured at 90° for 20 minutes and then placed at 130° for 3 h to obtain PDMS-g-PFA-CB.

4. Preparation of EP/PDMS-g-PFA-DB

The transparent, durable anti-icing EP/PDMS-g-PFA-DB coating was prepared using the following procedure. EP and HD were dissolved in tetrahydrofuran at a mass ratio of 3:1. The EP/HD solution was sprayed onto the glass substrate and left at 100°C for 3 mins to semi-cure the epoxy resin and form a substrate with a thickness of ~69 μm. The PDMS-g-PFA-DB solution was then sprayed onto the EP base and heated in an oven at 90°C for 3 hours, at which point the thickness was ~81 μm. When spraying, the distance between the gun nozzle and the sample is 20 ± 1 cm, the air pressure is 3.5 ± 0.05 bar, and 3 times. The preparation of EP/EFVS coatings is similar to the above procedure.

5. Preparation of SO/EP/PDMS-g-PFA-DB

20 μL of SO was sprayed on the EP/PDMS-g-PFA-DB coating and placed it at 60° in an oven to remove the solvent, after which the coating was left at room temperature for 24 h to obtain SO/EP/PDMS-g-PFA-DB.

6. Characterization

Fourier-transform infrared (FTIR) measurements in the frequency range 400–4000 cm-1 were conducted using a Nicolet FTIR 5700 spectrophotometer at room temperature. The films for the FTIR measurements were cast on KBr plates. Meanwhile, the 1H NMR spectra were recorded on a JEOL JNM-ECZ600R/S1 NMR spectrometer in deuterated solvents at room temperature. The molecular weight of the PDMS-g-PFA-DB was determined by gel permeation chromatography (GPC), using tetrahydrofuran as the eluent. Scanning electron microscopy (SEM) images were obtained using a Tescan Maia 3 scanning electron microscope. Prior to measurements, the sample surfaces were sputtered with Au. The transparency of the coating was characterized using Shimadzu UV-3600i Plus. K9 glass was used as a blank to reject the effect on transmittance. The glass transition temperature was tested using a NETZSCH DSC 200 F3 differential scanning calorimetry (DSC) analyzer under nitrogen atmosphere at a ramp rate of 10 degrees per minute. Topological network

solidification transition temperature test by TMA450EM with a pressure of 0.1N. The mechanical properties of PDMS-g-PFA-DB were tested by nanoindentation G200. The average values of modulus and hardness were calculated using data from 300-1000 nm. The adhesion strength of EP/PDMS-g-PFA-DB coating was obtained by MTS E44.104 universal testing machine with a tensile speed of 1mm/min. The CAs and SAs of the EP/PDMS-g-PFA-DB were measured by water contact angle measurement Sindin SDC-350 at room temperature with a 5 μL droplet.

The durability of the coating is characterized by sand dropping and water impacting tests. The sand dropped from a height of 30 cm at a rate of 50 g/min, with 50 g being one time. In water impacting test, the coating was fixed on the test bench at an inclination angle of 45°, and the deionized water with a flow rate of 1.1 m/s used for the impact experiment stuck the substrate from a height of 25 cm at 35 kPa. The impact process lasted for 4 h, with a total of 720 ± 2.5 L of water.

Shown below is a description of the ice adhesion test. The substrate was overlaid with a cuboid cuvette with a side length of 1 cm. The cuvette was then filled with deionized water. We next put the cuvette and substrate into a cold room at -15 °C for 24 hours to create an icicle. The test sample was then moved at a speed of 0.1 mm/s toward the force gauge. The adhesion stress was computed following the maximal force at the detachment site and the iced area.

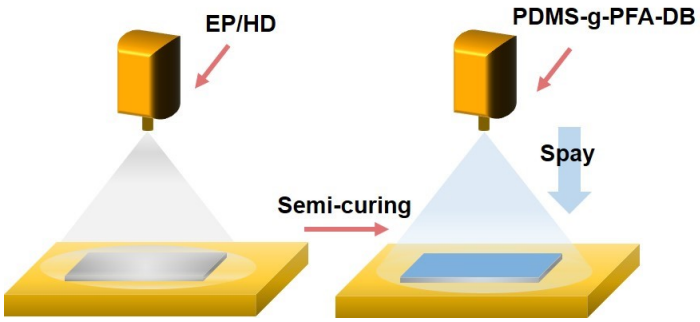

Fig. S1 Fabrication route of EP/PDMS-g-PFA-DB.

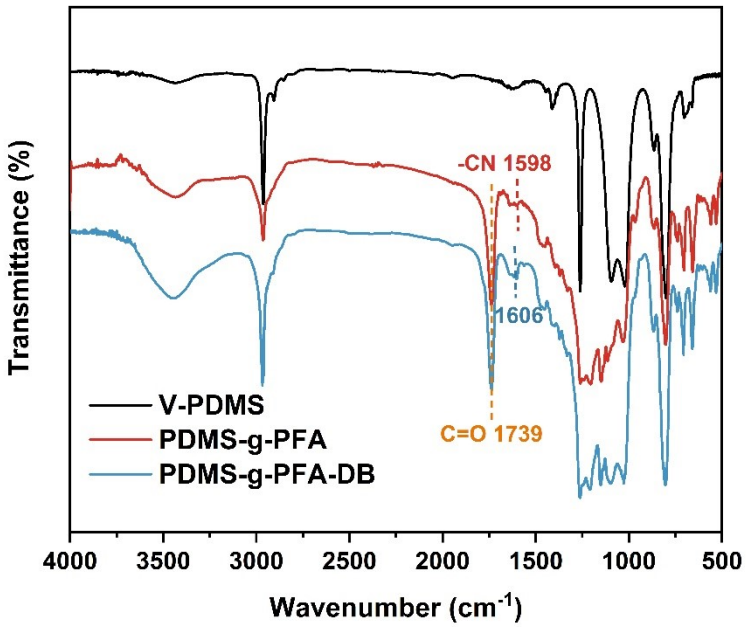

Fig. S2 FTIR spectra of the V-PDMS, PDMS-g-PFA and PDMS-g-PFA-DB.

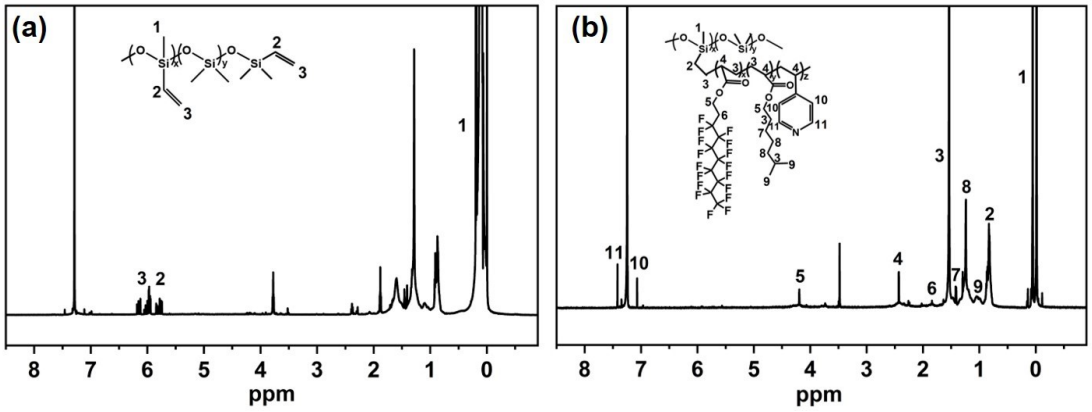

Fig. S3 [1] H NMR spectra of the (a) V-PDMS and (b) PDMS-g-PFA

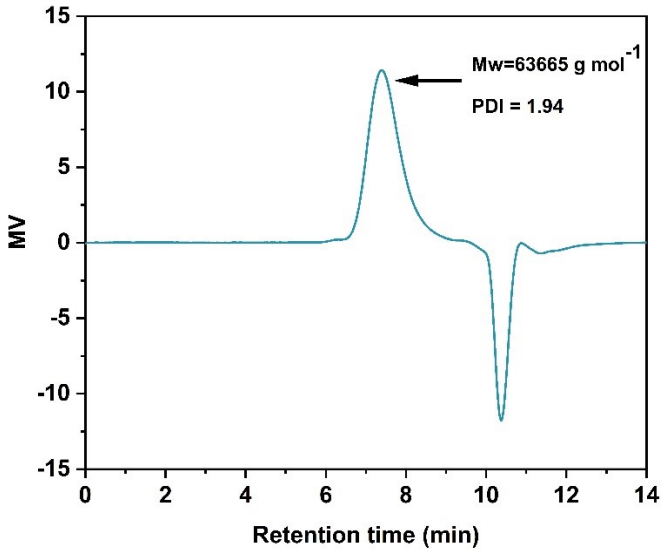

Fig. S4 Gel permeation chromatography of PDMS-g-PFA-DB

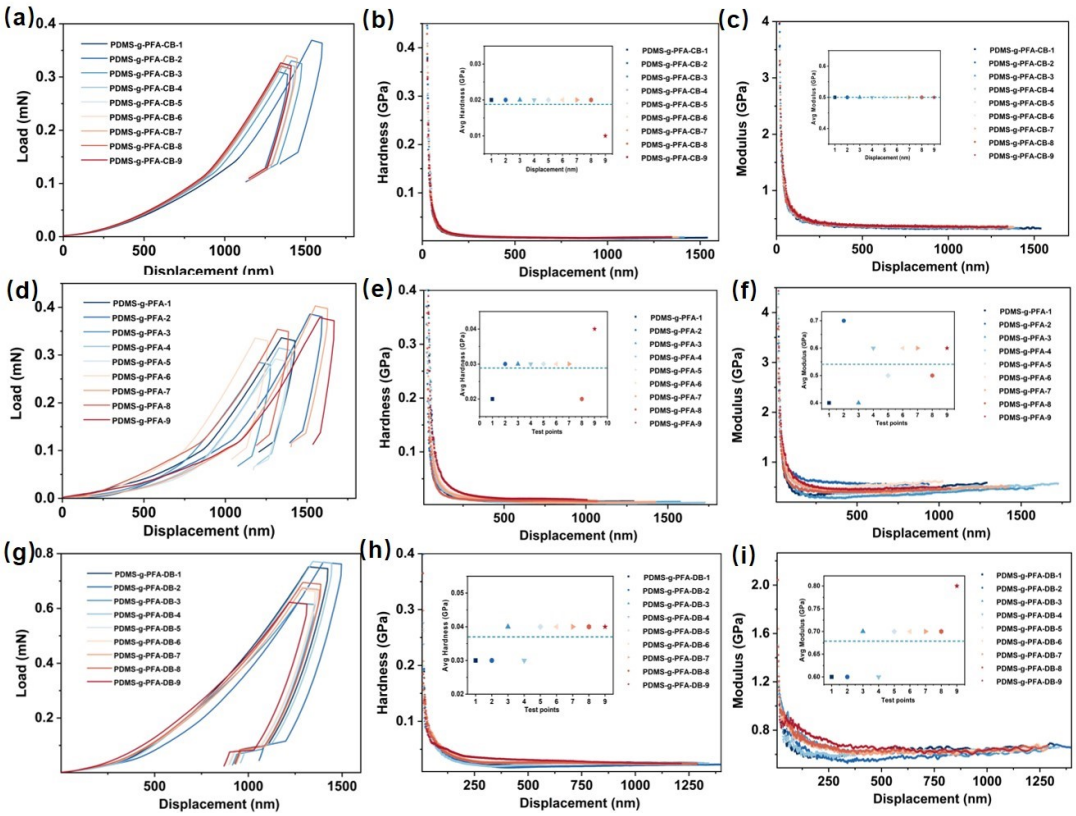

Fig. S5 (a) Load-displacement curves, (b) hardness-displacement curves and (c) elastic modulus-displacement curves of EFVS; (d) load-displacement curves, (e) hardness-displacement curves and (f) elastic modulus-displacement curves of VEFVS; (g) load-displacement curves, (h) hardness-displacement curves and (i) elastic modulus-displacement curves of PDMS-g-PFA.

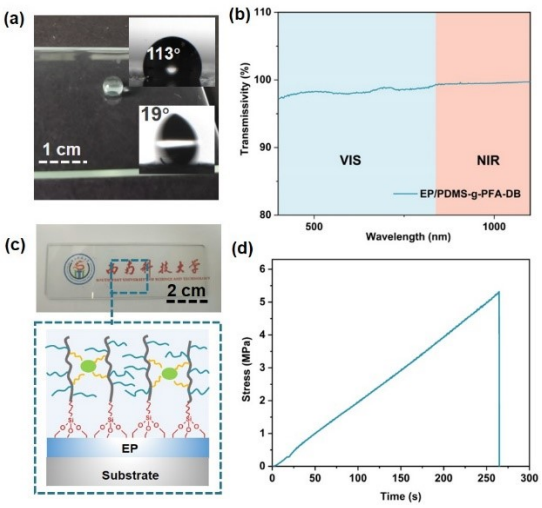

Fig. S6 The CA and SA of EP/PDMS-g-PFA-DB; (b) the transmittance of EP/PDMS-g-PFA-DB in 400-1100 nm; (c) the anchoring groups enhance the adhesion of coating; (d) the adhesion strength of the EP/PDMS-g-PFA-DB coating

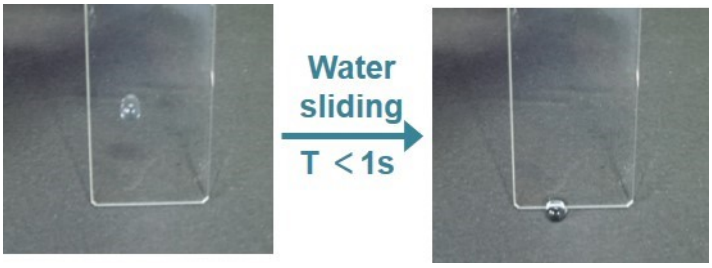

Fig. S7 Snapshots of water sliding on EP/PDMS-g-PFA-DB with a tilt angle of 19°.

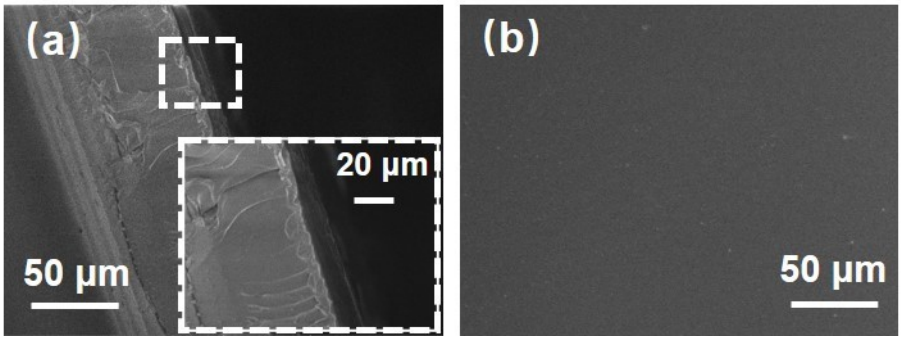

Fig. S8 SEM images of (a) cross section and (b) surface for EP/PDMS-g-PFA-DB

Table S1a. Coating thickness at different concentrations of epoxy resin and times of spraying (volume of 1.5 mL per spray)

Concentrations	Spraying times	Thickness
20 wt%	2	26±2 μm
20 wt%	3	39±4 μm
30 wt%	2	44±3 μm
30 wt%	3	69±2 μm

Table S1b. Coating thickness at different concentrations of PDMS-g-PFA-DB and times of spraying (volume of 1.5 mL per spray)

Concentrations	Spraying times	Thickness
5 wt%	2	7±1 μm
5 wt%	3	12±1 μm
10 wt%	2	11±2 μm
10 wt%	3	19±1 μm

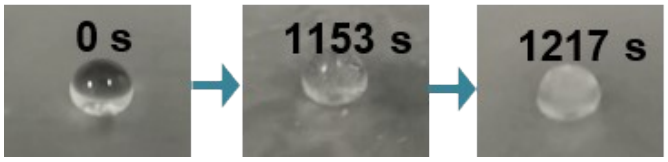

Fig. S9 Static anti-icing optical photographs based on EP/PDMS-g-PFA-DB at -10.0 °C.

Table S2. Comparison of delayed freezing time and ice adhesion of recently reported icephobic materials.

c	Temperature (°C)	Ice adhesion strength (kPa)	Delayed freezing time (s)	CA (°)	Reference
APP-treated silicone rubber surfaces	-10	32.9	-	＞150	1
Slippery LC surface	-10	20	-	-	2
PVDF/CNT coatings	-20	13.2	584	163	3
DLIL-SLIPS	-18	7.16	-	143	4
HPMC/SiO2 coating	-20	-	1366	161	5
C-18	-15	5.72	613	173	6
SLIPS	-18	20	-	100	7
SLPS	-10	7	697	107	8
L-P2′-g-PDMS	-10	0.4	-	67	9
stripe-VO_2/PDMS	-15	24.7	764	165	10
PVP−PDMS composite coating	-15	18	178	98	11

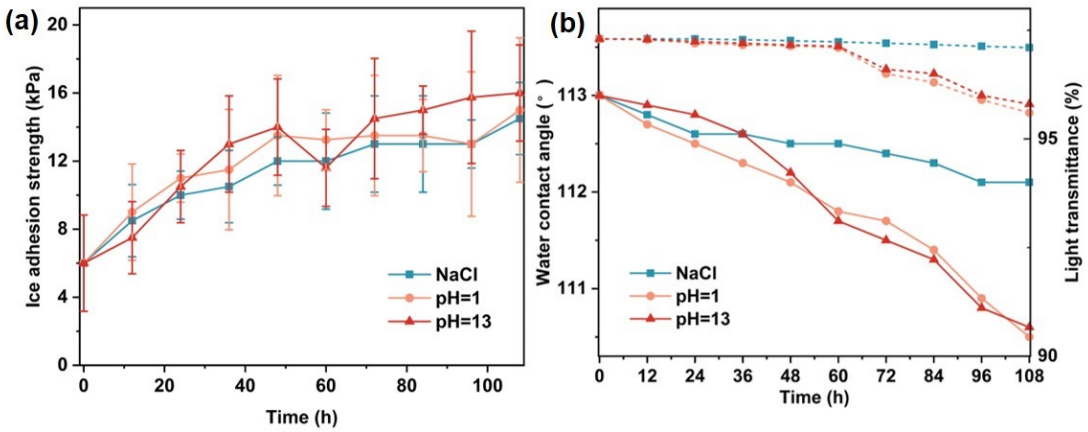

Fig. S10 (a) ice adhesion strength, (b) CAs and light transmittance variations of EP/PDMS-g-PFA-DB in saturated sodium chloride solution, pH=1 sodium hydroxide solution and pH=13 hydrogen chloride solution.

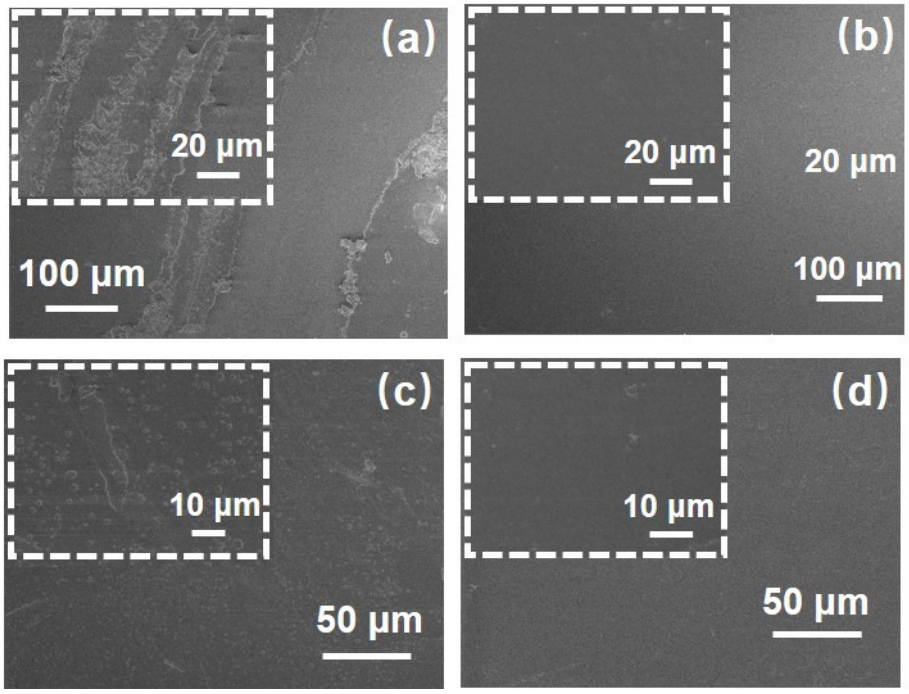

Fig. S11 SEM images of EP/PDMS-g-PFA-DB (a) being damaged by de-icing abrasion ; (b) recovering at 90 °C for 30 min; (c) being impacting by sand and (d) recovering at 90 °C for 30 min.

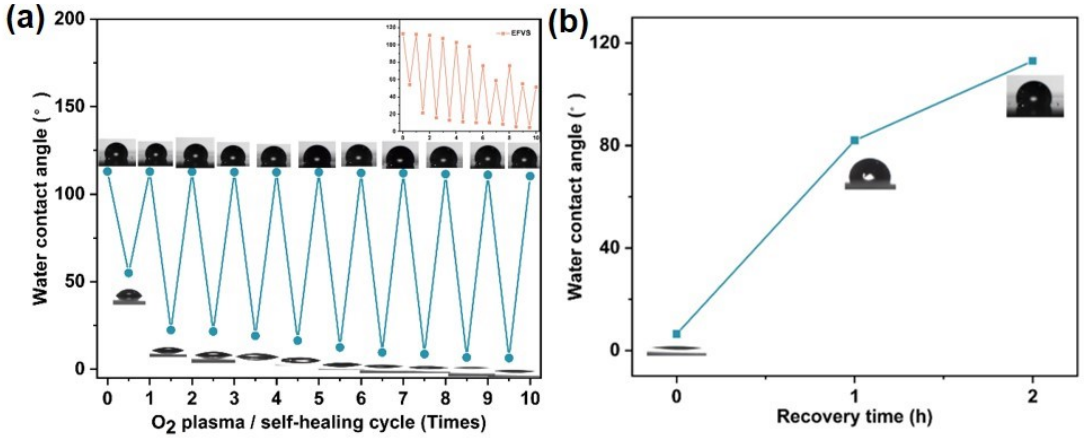

Fig. S12 (a) reversible changes of CAs for EP/PDMS-g-PFA-DB during plasma/self-healing cycles; (b) plot of CA vs. recovery time for EP/PDMS-g-PFA-DB at 90 °C.

Reference

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