

Supplementary Information

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Figure S9. FT-IR spectra of the samples with varied Span-80 concentration.

Scheme S1. Schematic illustration of the fabrication of superhydrophobic coating.

Experimental Procedures

Materials. Divinylbenzene (DVB), vinylbenzyl chloride (VBC), boron fluoride ethyl ether (BFEE) and sorbitan oleate (Span-80) were purchased from Sigma-Aldrich. Heptane, ethanol and acetone were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. (SCRC). Epoxy resin F46 was supplied by the Shanghai Resin Factory. All chemicals were purchased and used as received.

Characterization. Scanning electron microscopy (SEM) measurement was performed with a HITACHI S-4800 apparatus operated at an accelerating voltage of 15 kV. The samples were ambient dried and vacuum sputtered with Pt. Energy dispersive X-ray (EDX). Analysis was performed with a Hitachi S-4800 scanning electron microscope (SEM) equipped with an EDX analyzer operated at an accelerating voltage of 15 kV. Internal morphologies were characterized using JEM-1011 TEM operated at an acceleration voltage of 100 kV. Morphologies of the stabilized BFEE droplets were characterized using Leica DMLP microscope. Contact angle of 5 μ L of water droplets was measured on Dataphysics OCA20 at ambient temperature. Thermal conductivity of the prepared samples was measured at room temperature using 3 ω harmonic measurement system developed by Institute of Engineering Thermophysics, Chinese academy of sciences.

Preparation of the PDVB HHPs: For a typical example, at room temperature e.g. 25 °C (all reactions were performed at room temperature unless otherwise noted), 150 mg of BFEE (boron trifluoride diethyl etherate complex $\text{BF}_3 \cdot \text{O}(\text{Et})_2$) was immediately added into 150 mL of heptane containing 0.1 wt.-% of surfactant, Span-80, under ultrasound (40 KHz, 120 W), when the system was evenly dispersed after 2 min, 2.0 wt.-% of the DVB monomer was added to begin the cationic polymerization, the reaction proceeded for 15 min under ultrasound until terminated by adding a terminator (i.e. ethanol). In order to monitor growth of the HHPs at different stage, 10 g of ethanol was added to terminate the polymerization at specific reaction steps. The samples were filtered and washed with ethanol to remove residual initiator, monomer and surfactant. After residual ethanol was evaporated, the HHPs powder was obtained.

Preparation of the Poly (DVB-co-VBC) segment-HHPs: The first step was the same as the preparation of PDVB HHPs, the polymerization of first monomer DVB at a concentration of 0.7 wt.-% occurred for 10 min, the second monomer VBC was then mixed with DVB at a ratio of 1:2 at a concentration of 0.7 wt.-% was added to the system, the polymerization then proceeded for another 10 min, and finally was terminated by adding 10 g of ethanol. The samples were filtered and washed with ethanol to remove residual initiator, monomers and surfactant. After residual ethanol was evaporated, the Poly (DVB-co-VBC) block-hairy particles powder was obtained.

Fabrication of superhydrophobic coatings: Curable epoxy resin F-46 (0.5 g) was first dissolved in acetone (2.0 g), and spun on to a glass or fabric substrate by spin coating, after the solvent was evaporated, the reactive hairy particles were deposited onto the epoxy layer and kept at room temperature for 30 min to ensure that the epoxy had been cured. The coated substrate was then washed by ethanol to remove any free particles, and dried at ambient temperature. Finally, the hairy particles were tightly fixated, achieving a robust coating.

Supplementary Figures

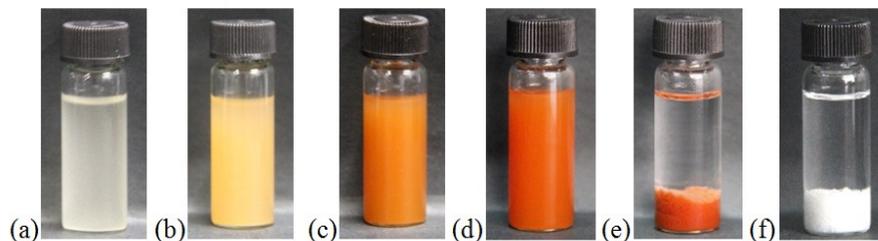


Figure S1. Macroscopical colour evolution of the reaction system at 2.0 wt.-% of monomer, 0.1 wt.-% of BFEE, 0.1 wt.-% of Span-80, at varied polymerization time (min) of: a) 0.5; b) 2; c) 5; d) 10; e) the precipitation of sample (d); f) deactivated sample after adding ethanol.

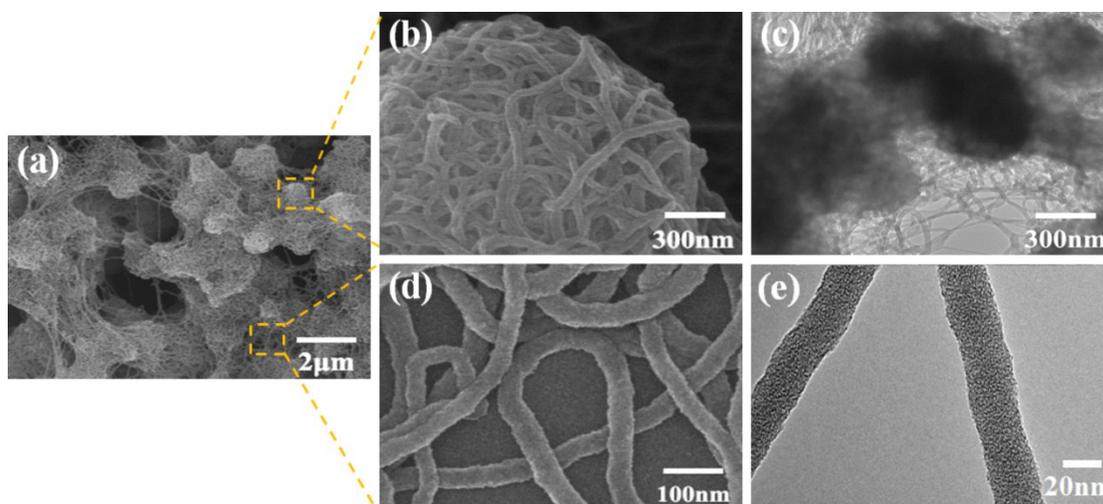


Figure S2. a), b),c) Morphologies and microstructures of HHPs synthesized at 2.0 wt.-% of monomer, 0.1 wt.-% of BFEE, 0.1 wt.-% of Span-80, respectively; polymerized for 10min; d), e) SEM and TEM images of hairs (nanofibers) of the obtained HHPs.

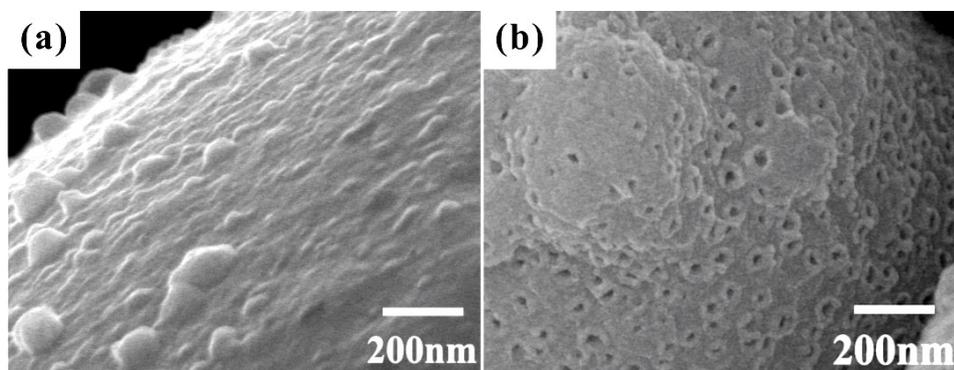


Figure S3. SEM images of the particles' surface obtained after (a) and before (b) formation of buds.

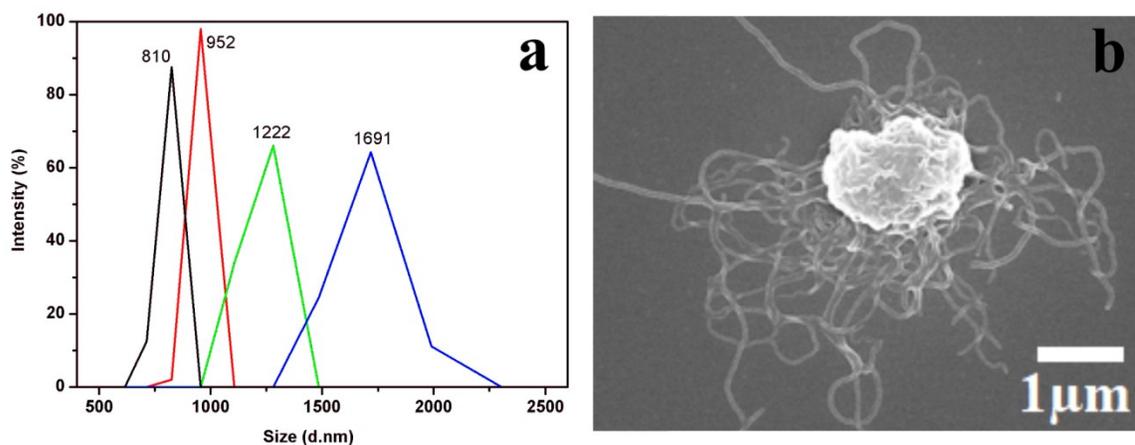


Figure S4. a) DLS diagrams of HHPs at different polymerization time (min) dispersed in ethanol: 2 (black); 5 (red); 7 (green); 10 (blue); at 2.0 wt.-% of DVB, 0.1 wt.-% of BFEE, 0.1 wt.-% of Span-80; b) SEM image of single HHP, obtained from sample dispersed in toluene at a very low concentration (0.001 wt.-%).

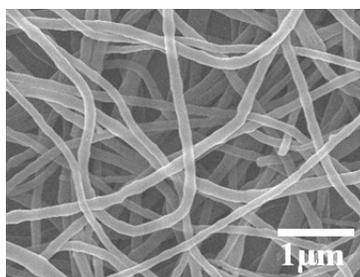


Figure S5. SEM images of the nanofibers obtained without Span-80, at concentration of 0.1 wt.-% of BFEE, 2 wt.-% of DVB, polymerized for 10 min.

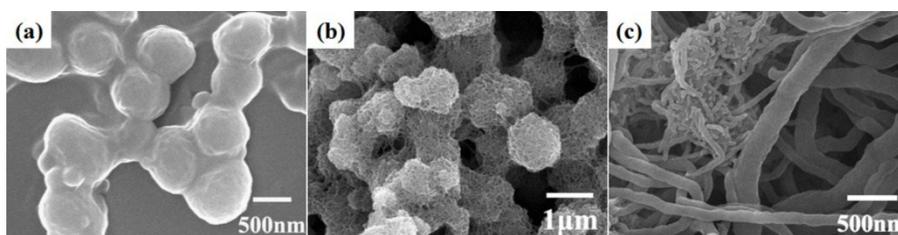


Figure S6. SEM images of the samples obtained at varied amounts of BFEE (wt.-%): a) 0.02; b) 0.05; d) 0.20, with concentration of 2.0 wt.-% of DVB, 0.1 wt.-% of Span-80, polymerized for 20 min.

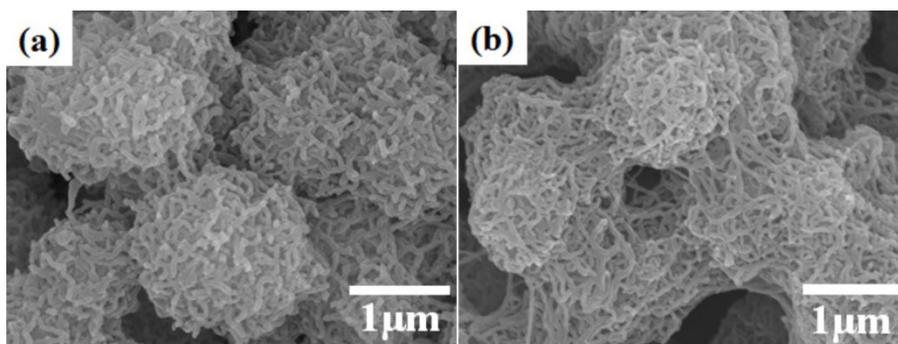


Figure S7. a) Poly (DVB) HHPs synthesized at concentration of 0.7 wt.-% of DVB, polymerized for 10 min. b) Poly (DVB-co-VBC) HHPs obtained by continued polymerization by adding 0.7 wt.-% of VBC/DVB mixture (2:1) and reacted for another 10 min.

a			b			c		
Element	Weight%	Atomic%	Element	Weight%	Atomic%	Element	Weight%	Atomic%
CK	99.63	99.87	CK	99.20	99.73	CK	99.22	99.74
ClK	0.37	0.13	ClK	0.80	0.27	ClK	0.78	0.26
Totals	100.00		Totals	100.00		Totals	100.00	

d			e			f		
Element	Weight%	Atomic%	Element	Weight%	Atomic%	Element	Weight%	Atomic%
CK	97.16	99.02	CK	96.09	98.64	CK	96.97	98.95
ClK	2.84	0.98	ClK	3.91	1.36	ClK	3.03	1.05
Totals	100.00		Totals	100.00		Totals	100.00	

g			h			i		
Element	Weight%	Atomic%	Element	Weight%	Atomic%	Element	Weight%	Atomic%
CK	96.24	98.70	CK	95.68	98.49	CK	94.82	98.18
ClK	3.76	1.30	ClK	4.32	1.51	ClK	5.18	1.82
Totals	100.00		Totals	100.00		Totals	100.00	

Figure S8. Cl element distribution along one nanofiber as shown in Figure 3b, characterized by dispersive X-ray spectrometer (EDS).

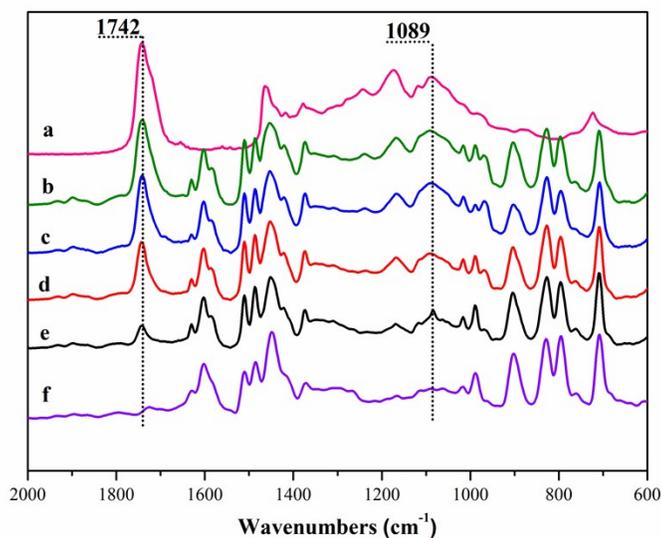
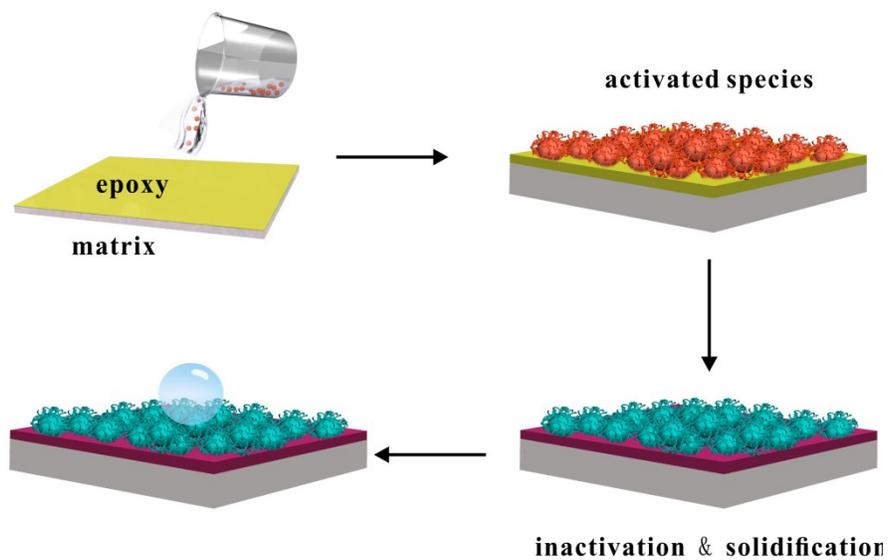


Figure S9. FT-IR spectra of the samples obtained at varied Span-80 concentrations (wt.-%): a) 0; b) 0.02; c) 0.05; d) 0.1; e) 0.2. f) FT-IR spectrum of Span-80. The characteristic band at 1742 cm^{-1} is assigned to carbonyl group, and 1089 cm^{-1} is assigned to the C-O-C stretching vibration of Span-80.



Scheme S1. Schematic illustration of the fabrication of superhydrophobic coatings.