Supporting Information

Robust superamphiphobic coatings in confined and chemically inert tubular geometries enabled by a dynamic circulation coating strategy

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Experimental Section

Materials

Tannic acid (TA, 99.9%), dopamine (DA, 99.0%), tris(2-carboxyethyl)phosphine (TCEP) and azobis(2-methylpropionitrile) (AIBN, 99.0%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China. Trichlorovinylsilane (TCVS, 97.0%) was bought from Gelest. SiO_2 microparticles were supplied by Jiangsu Lianrui New Material Co., Ltd. Other reagents including 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (PFDT, 99.0%), anhydrous ethanol, *n*-propanol, toluene, acetone, and *N*,*N*-dimethylformamide (DMF) were purchased from China National Medicines Co. Ltd. All the chemical reagents were used as received without further purification. Polypropylene (PP) plates (500 mm × 500 mm × 3 mm) were purchased from Dongguan Feitai Metal Products Co. Ltd, China, and were cut into small pieces (60 mm × 20 mm). The other substrates were obtained from our lab or purchased from local markets. All the substrates were cleaned with anhydrous ethanol and acetone, deconned by ultrasonication at 37 kHz and 25 °C for 30 min, and finally dried with an N_2 flow.

Preparation of TDSP/SNFs/PFDT coatings

First, 0.10 g of TA, 0.20 g of DA, and 0.10 g of SiO_2 microparticles (10 μm) were dissolved or dispersed in 100 mL of deionized water, followed by ultrasonication for 2 min to form a homogeneous precursor dispersion. Subsequently, the pH of the dispersion was adjusted to 8.5 by adding 0.64 g of tris(hydroxymethyl)aminomethane (Tris). To fabricate the coating on different substrates, the PP plate was then immersed in the dispersion, or the dispersion was pumped into a PP tube (6 mm in inner diameter and 10 cm in length) using a peristaltic pump with a precisely controlled flow rate of 0.5 mL/s, and the reaction was allowed to proceed for 6 h at ambient temperature. Finally, the resulting TDSP coating was dried in an oven at 70 °C.

Subsequently, the water content in toluene (80 mL) was precisely adjusted to 200±10 ppm by purging with dry and wet N_2. Then, 200 μL of TCVS was added into toluene at room temperature. The TDSP coating was subjected to this solution via either static immersion or dynamic pumping with a precisely controlled flow rate 0.05 mL/s, facilitating the self-assembly of SNFs on its surface. After reacting for 12 h, the resulting TDSP/SNFs coating was rinsed successively with 15 mL of toluene and 15 mL of ethanol, and finally dried in an oven at 70 °C.

Finally, to introduce a low-surface-energy material via click chemistry, 1.20 mL of PFDT was added to 20 mL aliquots of four different solvents: *n*-propanol, ethanol, toluene, and DMF. Subsequently, 0.06 g of AIBN as an initiator and 0.04 g of TCEP as a stabilizer were added into each solution and thoroughly dissolved. The TDSP/SNFs coating was then immersed in the reaction solution at 70 °C for 6 h to facilitate a thorough thiol-ene click reaction between the thiol groups (-SH) of PFDT and the vinyl groups on the SNFs. Upon completion of the reaction, the resulting TDSP/SNFs/PFDT coatings were rinsed copiously with 15 mL of anhydrous ethanol and oven-dried. The coatings were denoted as $TDSP/SNFs/PFDT_{plate}$ and $TDSP/SNFs/PFDT_{tube}$ according to the shapes of the PP substrates. Following an identical procedure, analogous TDSP/SNFs/PFDT coatings were also fabricated on other substrates.

Hydrostatic pressure resistance test

The resistance of the coatings to high hydrostatic pressure was evaluated using a custom-designed stainless steel pressure vessel. The coated substrate (either plate or tube) was placed horizontally inside the vessel and fully immersed in deionized water. The vessel was then sealed, and high-purity N_2 was introduced to pressurize the system to the target levels of 1.0 MPa, 1.5 MPa, or 2.0 MPa. After the designated immersion period, the pressure was carefully released, and the sample was rapidly extracted from the vessel. To minimize any potential effects of evaporation or surface drying, the sample was transferred to the contact angle goniometer within 20 s, and its CA and SA were measured immediately to capture the state directly resulting from the pressure exposure. For samples that were wetted, they were dried in an oven at 60 °C for 30 min, and their wettability was re-measured.

Dynamic pressure resistance test

To investigate the coating's resistance to droplet impact, 10 μL water droplets were dropped onto its horizontal surface from heights of 1 cm, 0.75 m, 1 m, and 2 m. The entire process was visualized at 4,000 fps using a high-speed video camera (FASTCAM, Mini UX100).

Characterization

The CA and SA of various liquids (10 μL) were measured at ambient temperature using an optical video CA instrument (OCA20, Dataphysics, Germany). The surface morphology of samples was observed by a field emission scanning electron microscope (SEM, TESCAN MIRA LMS) equipped with an energy dispersive spectrometer. For SEM observation, all the samples were fixed on copper roots and coated with gold (~7 nm). The XPS spectra of samples were recorded using a VG ESCALAB 250 Xi spectrometer equipped with a monochromatic Al Kα X-ray emitter and a hemispherical electron analyzer. The spectra were recorded in the constant energy mode of 100 eV, and all the binding energies were calibrated with the C 1s peak at 284.6 eV as the reference. The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of samples were recorded on a Bruker model VERTEX 70 infrared spectrometer.

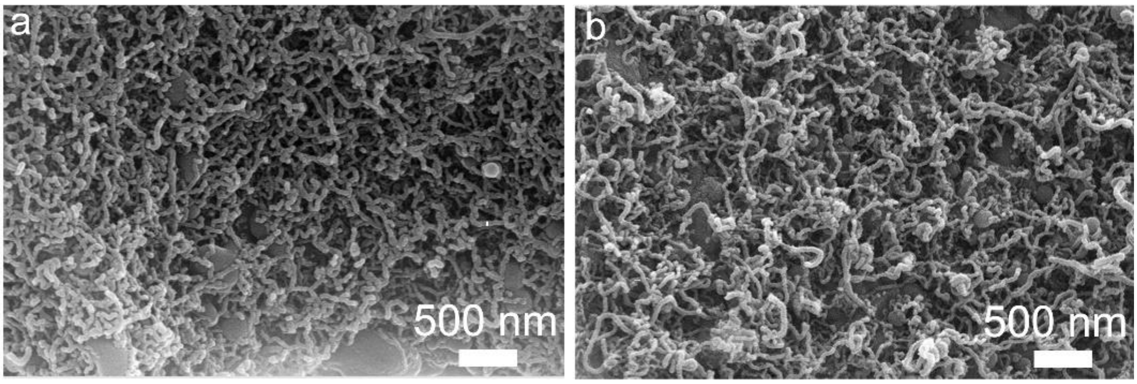

Fig. S1 SEM images of the (a) TDSP/SNFs coating and (b) TDSP/SNFs/$PFDT_{plate}$ coating.

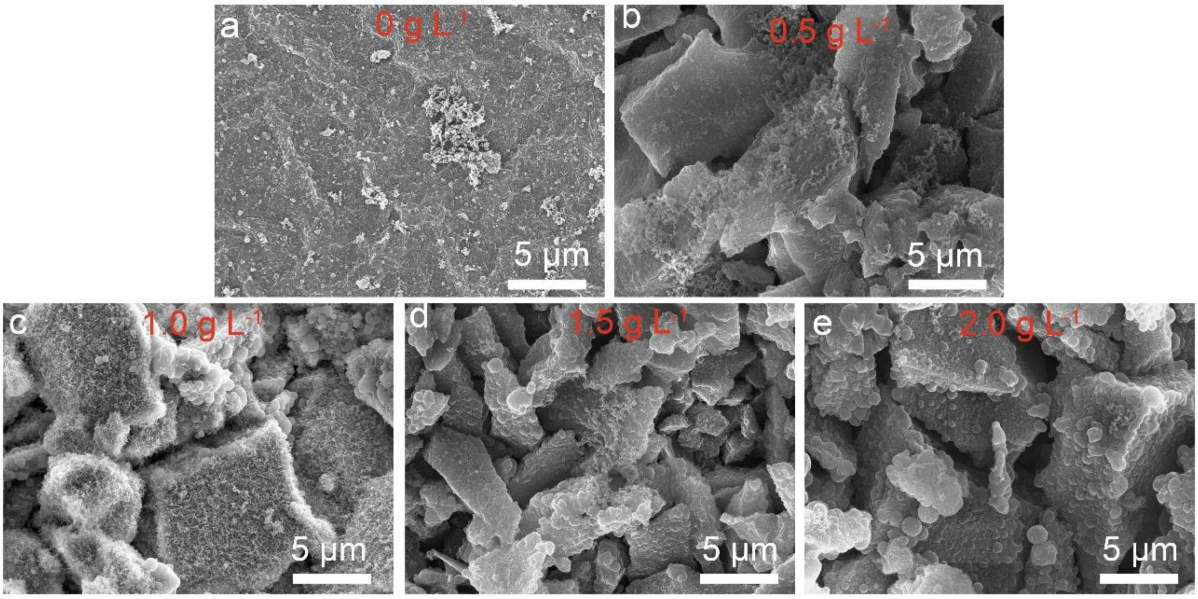

Fig. S2 (a-e) SEM images of the TDSP/SNFs/$PFDT_{plate}$ coatings with different SiO_2 content.

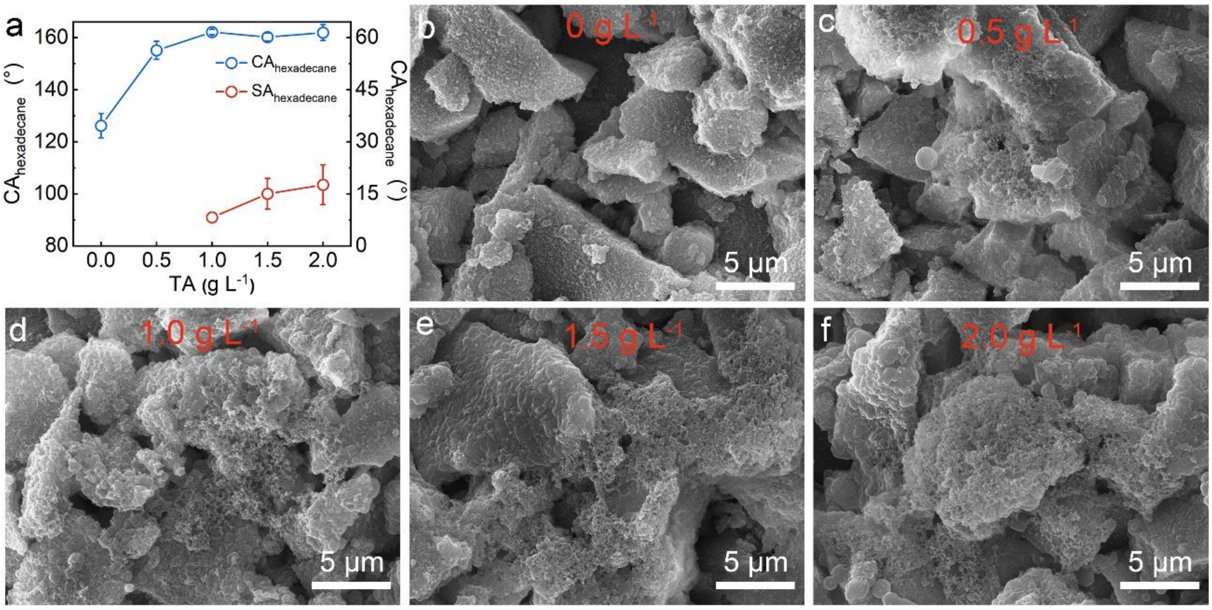

Fig. S3 (a) Variation of $CA_{n\text{-hexadecane}}$ and $SA_{n\text{-hexadecane}}$ of the TDSP/SNFs/$PFDT_{plate}$ coatings as a function of TA content and (b-f) the corresponding SEM images of the coatings. The data in (a) are shown as mean ± SD, n = 5.

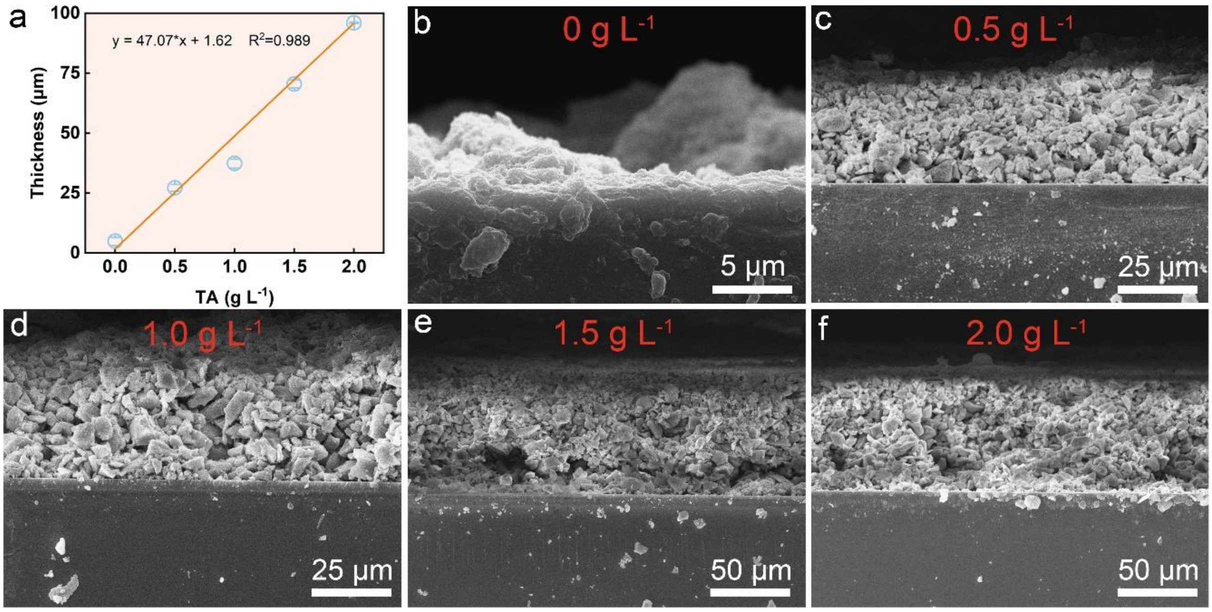

Fig. S4 (a) Changes in thickness of the TDSP/SNFs/$PFDT_{plate}$ coatings with TA content, and (b-f) the corresponding cross-sectional SEM images of the coatings. The data in (a) are shown as mean ± SD, n = 5.

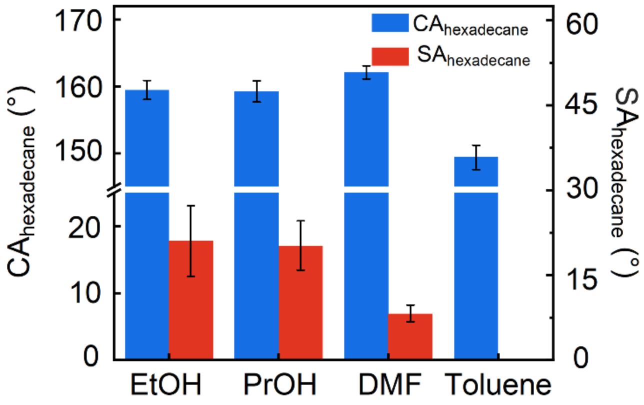

Fig. S5 Effects of solvents in the thiol-ene click reaction on superamphiphobicity of the TDSP/SNFs/PFDT$_{plate}$ coatings.

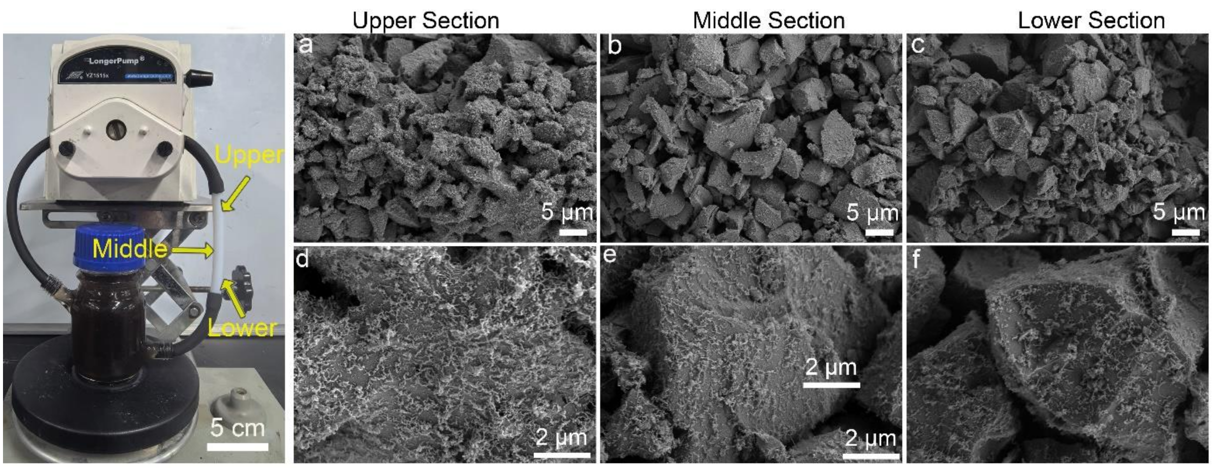

Fig. S6 SEM images of the TDSP/SNFs/PFDT$_{tube}$ coating on (a, d) upper, (b, e) middle and (c, f) lower section of PP tube.

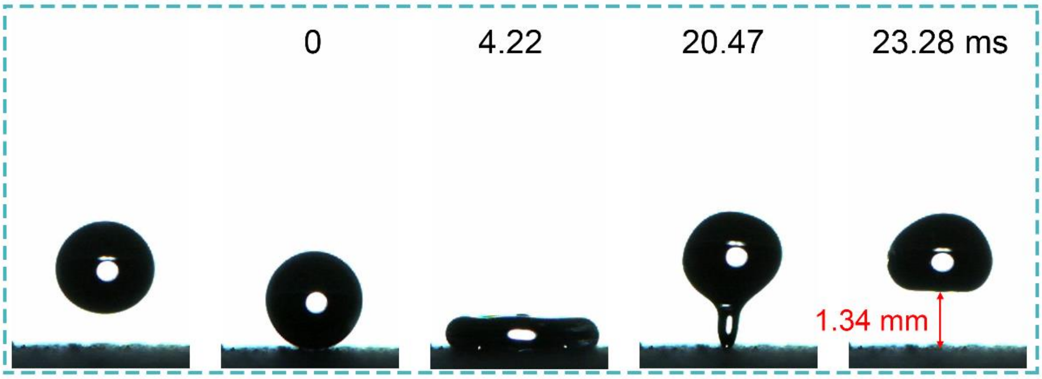

Fig. S7 The first bounce of the hexadecane droplet (10 μL) released from 10 mm height on the TDSP/SNFs/$PFDT_{plate}$ coating.

Table S1 Elemental contents of the TDSP, TDSP/SNFs and TDSP/SNFs/PFDT coatings.

Elemental content (%)	TDSP	TDSP/SNFs	TDSP/SNFs/PFDT
Si	62.30	35.49	33.58
O	32.83	35.58	36.91
C	4.87	28.93	26.50
N	0.01	0.01	0.39
F	-	-	2.62
S	-	-	0.01

Table S2 Comparison of superamphiphobicity of the TDSP/SNFs/PFDT$_{tube}$ coating with reported coatings in tubes.

Material composition	Substrates	Shape	Superhydrophobic/superamphiphobic property	Refs.
SNFs	PP/PE/PTFE	Plate (2.4*5 cm)	CA_{water} = 163°, SA_{water} = 2° $CA_{soybean\ oil}$ =154°, $SA_{soybean\ oil}$ <30°	This work
SNFs	PP/PE/PTFE	Tube (aspect ratio 100:6)	CA_{water} = 163°, SA_{water} = 2° $CA_{soybean\ oil}$ =154°, $SA_{soybean\ oil}$ <30°	This work
PDMS	Al rods	Tube (aspect ratio 900:6)	CA_{water} = 155°, SA_{water} = 8°	[1]
Titania nanotube arrays	Titania	Tube (aspect ratio1000:6)	CA_{water} = 166°, SA_{water} = 2° $CA_{glycerol}$= 163°, $SA_{glycerol}$= 3°	[2]
Nanoparticle aerosols	Glass	Tube (aspect ratio 90:6)	$CA_{dodecene}$ > 163°, $SA_{dodecene}$ < 10°	[3]
SNFs	LDPE	Tube (aspect ratio 2000:1)	The drops showed very low adhesion	[4]
SNFs	Glass	Tube (aspect ratio 70:28)	CA_{water} ~166°, SA_{water} ~ 2°	[5]

Table S3 Comparison of static pressure resistance of various superhydrophobic/superamphiphobic coatings.

Material/Morphology	Static pressure resistance		Refs.
	Test conditions	Results	
SNFs	1 MPa	After 72 h, CA>150°, SA<10°	This work
Anodized Ti alloy	1 cm (~0.098 kPa)	After 208 d, Cassie-Baxter state	[6]
Carbon nanofiber/SiO_2	80 cm (~7.8 kPa)	After 28 d, CA=150°, SA=18°	[7]
Candle soot	80 cm (~7.8 kPa)	After 38 d, CA>150°, SA<10°	[8]
Micro and nanohairs	350 kPa	After 4 h, surface dry	[9]
PP microparticles+SiO_2 nanoparticles	3 MPa	After 12 h, surface dry	[10]
Microshell and nanoseeds	6 MPa	After 72 h, CA>150°, SA<10°	[11]

Table S4 Friction forces of liquid droplets on superamphiphobic coatings.

Samples	Liquid	Drop volume (μL)	SA (°)	Friction force (μN)
$TDSP/SNFs/PFDT_{plate}$	water	10	1.0	1.71
$TDSP/SNFs/PFDT_{tube}$	water	10	2.0	3.42

Movie S1 Impact of a water droplet (10 μL) released from 1 m height on the $TDSP/SNFs/PFDT_{tube}$ coating (Frame rate: 4,000 fps).

Movie S2 Elastic positive collision of a water droplet (10 μL) released from 0.75 m height on the $TDSP/SNFs/PFDT_{tube}$ coating (Frame rate: 4,000 fps).

Movie S3 Elastic oblique collision of a water droplet (10 μL) released from 0.75 m height on the $TDSP/SNFs/PFDT_{tube}$ coating (Frame rate: 4,000 fps).

Movie S4 Rolling process of a 10 μL water droplet on the $TDSP/SNFs/PFDT_{tube}$ coating (Frame rate: 4000 fps).

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