Electronic Supplementary Information

Underwater superoleophobic coatings fabricated from tannic acid-decorated carbon nanotubes

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Experimental Section

Materials: Multi-walled carbon nanotubes (MWCNTs) were purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences (>95% purity) with outer diameter of 8-15 nm and length of 50 μ m. Tannic acid (TA) was obtained from Aladdin China with a structure characterized as in Fig. S1. It has a large number of phenolic hydroxyl groups with a molecular weight of 1701 (C₇₆H₅₂O₄₆). The microporous polypropylene membrane (MPPM) is a commercial product of Membrana GmbH (Germany) (mean pore size 0.2 mm, porosity 75%).



Fig. S1 Molecular structure of tannic acid (TA).

Preparation of the TA-decorated MWCNTs coatings: 4 mg MWCNTs were added into a vial of 20 mL TA aqueous solution (50 μ g/mL) before 20 min sonication at frequency of 200 Hz for twice. The obtained TA-decorated MWCNTs dispersion was centrifuged at rate of 5000 rpm for 10 min. The supernatant was vacuum-filtered through a pre-wet MPPM to form a flat and uniform coating on the substrate. The as-prepared TA-decorated MWCNTs coating was then washed by distilled water to remove residual TA and dried in vacuum oven at 40 °C.

Preparation of the nascent MWCNTs coatings: Nascent MWCNTs were dispersed in a mixture of DMF and NMP at the ratio of 1:1 with the help of sonication. Vacuum filtration was then used to fabricate a uniform coating. It was immersed in ethanol for 1 h to remove remaining organic solvents and vacuum-dried at 40 °C before use.

Characterization: UV–vis spectrometer (UV 2450, Shimadzu, Japan) was used to measure the turbidity of dispersion. After sonication, MWCNTs dispersant was centrifuged at the rate of 5000 rpm for 10 min, with the supernatant being collected as sample. The measurement was conducted at 800 nm to quantify the turbidity of MWCNTs in aqueous phase. As TA has no absorbance at this point, there is a good correlation between the absorbance strength and the concentration of MWCNTs. ¹

Field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) was used to characterize the surface and cross-section morphology of the coatings. Samples were spurted with Au for 7 min to make them conductive for FESEM observation.

Chemical composition of the surface was analyzed by X-ray photoelectron spectroscopy (XPS, Perkin Elmer, USA) and a laser confocal Raman microspectroscopy (inVia

Reflex, Renishaw, UK). Samples were prepared as follow. First, the MWCNTs dispersant was washed by distilled water and centrifuged for several times to make sure there is no TA left in solution. Then, lyophilization was taken to obtain a solid powder sample. A sample of the nascent MWCNTs was set as control, obtained following the same procedure.

Transmission electron microscope (TEM, JEM-1200EX, Japan) was used to have a microscopic observation of a single strand of TA-decorated MWCNTs. Samples were made by dipping MWCNTs dispersion onto a piece of carbon-coated TEM grid before vacuum drying. Nascent MWCNTs was sampled following the same way, but with the dispersion in DMF/NMP.

The wettability of MWCNTs coating can be quantitatively characterized by water and oil contact angle (known as WCA or OCA) using a Drop Meter A-200 contact angle system (MAIST Vision Inspection & Measurement Co. Ltd., China) with water drop volume set at 2 μ L and oily drop at 5 μ L. The value of angle was averaged from three measurements. Underwater measurements were carried out in a homemade sink, with water or other aqueous solutions being filled to create a specific underwater environment.

Calculation of the modification degree of TA on MWCNTs: TA concentration can be quantified by UV-vis measurement at the wavelength of 275 nm.¹ The calibration curve is shown in Fig. S2, according to which the concentration of TA solution after MWCNTs decoration and vacuum filtration is calculated to be 21.9 mg/L. Considering the volume of TA solution is 20 mL and the TA concentration before test is 50 mg/L, 0.562 mg TA is adsorbed on 4 mg MWCNTs, that is, the mass ratio of TA versus MWCNTs in this modification is 140 mg/g.



Fig. S2 Calibration curve for TA concentration.



Fig. S3 XPS spectra of the nascent MWCNTs (a) and the TA-decorated MWCNTs (b).

	[0]	[C]	[O]/[C]
Nascent MWCNTs	5.15%	94.85%	0.054
TA-decorated MWCNTs	13.87%	86.13%	0.161

Table S1 Chemical composition of the TA-decorated and nascent MWCNTs.



Fig. S4 Core-level XPS spectra of O_{1s} on the nascent MWCNTs (Left) and the TA-decorated MWCNTs (Right).



Fig. S5 Raman spectra of the nascent MWCNTs (a) and the TA-decorated MWCNTs (b).



Fig. S6 (a) The TA-decorated MWCNTs coatings maintain original appearance after 24h scouring. The edge of the membrane wrinkled because the coated membrane was compressed into a round groove during the scouring test. (b) The TA-decorated MWCNTs coatings show hydrophilicity in air after scouring. c) The TA-decorated MWCNTs coatings keep their superoleophobicity underwater after scouring.

	WCA (°)	Underwater OCA (°)	
Ethanol	150.2 ± 3.7	The oil drop immersed into the surface within 1 second.	

Table S2 Wettability of TA-decorated MWCNTs coating after 20 mL solvents washing.

DMF	152.4 ± 0.5
NMP	162.9 ± 0.2
Acetone	146.7 ± 5.0
Toluene	150.0 ± 5.7

Table S3 Wettability of solvent-treated MWCNTs coating after 20 mL TA (50 mg/L)filtration.

	WCA (°)	Underwater OCA (°)
Ethanol	27.8 ± 2.5	161.1 ± 7.8
DMF	41.1 ± 0.9	163.2 ± 1.8
NMP	34.0 ± 0.2	157.8 ± 2.6
Acetone	59.6 ± 1.3	152.8 ± 3.3
Toluene	48.3 ± 1.4	156.3 ± 6.2

Reference

1. D. Lin, N. Liu, K. Yang, L. Zhu, Y. Xu and B. Xing, *Carbon*, 2009, **47**, 2875-2882.