Supporting Information for

Construction of Superhydrophilic and Under-water Superoleophobic Carbon-Based Membranes For Water Purification

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Fig. S1 Photograph of oil droplets (dichloromethane, carbon tetrachloride) sits on the Ag/PAA-CNTs hybrid membrane, the oil droplet was stained with oil red for clear observation.



Fig. S2 Cross-sectional SEM image of (A) a Ag/PAA-CNTs hybrid membrane and (B) the further amplification of the hybrid membrane surface.



Fig. S3 XPS spectra of (A)C_{1s} spectrum of CNTs membrane,(B)O_{1s} spectrum of CNTs membrane, (C)C_{1s} spectrum of PAA-CNTs membrane, (D)O_{1s} spectrum of PAA-CNTs membrane.



Fig. S4 (A) FT-IR spectra of (a) CNTs, (b) PAA-CNTs, (c) Ag/PAA-CNTs; (B) TGA curves of (a) CNTs, (b) PAA-CNTs, (c) Ag/PAA-CNTs.

The attachment of PAA was also confirmed by FTIR. As shown in Fig. S4, the absorption peak at 3445 cm⁻¹ and 1640 cm⁻¹ in the FTIR spectrum of CNTs corresponded to the characteristic -OH bonds stretching vibrations and C=C bonds stretching vibrations, respectively. After PAA modification, red shift of the -OH and C=C bands of PAA-CNTs is observed, which are attributed to the weaker mutual electronic interaction between CNTs after modification, indicating the covalent side-wall functionalization of CNTs. TGA was applied to determine the relative amount of CNTs, PAA-CNTs, Ag/PAA-CNTs, respectively. As shown in Fig. S4 (B), the weight loss corresponding to the pristine purified CNTs at 800 °C under nitrogen is 3.2 wt %.

For the sample of PAA-CNTs, two main weight-loss regions are found. The first weight-loss region may be assigned to the decomposition of carboxyl groups of PAA on the surface of CNTs, and the significant weight reduction in the second region is likely due to the decomposition of the polymer backbone and hydroxyethyl groups. A similar phenomenon has been reported before.^{1,2} Compared with CNTs, PAA-CNTs, the weight loss of the Ag/PAA-CNTs nanocomposites below 200°C is much lower, indicating that main oxygen-containing functional groups of CNT has been converted after reduction. Moreover, the weight loss associated with high temperature pyrolysis of Ag/PAA-CNTs.

The emulsion droplets before and after filtration were monitored by DLS and optical microscopy images (**Fig. S5, Fig. S6**). The droplet size distribution for water-in-chloroform and water-in-hexane emulsions are around 300 nm, 300 nm, respectively. After filtration, droplets size greater than 10 nm is not observed.



Fig. S5 DLS and optical microscopy images of the feed emulsions (up, A and B) and their filtrate correspondingly (down, C and D) for surfactant-stabilized chloroform-in-water emulsions.



Fig. S6 DLS and optical microscopy images of the feed emulsions (up, A and B) and their filtrate correspondingly (down, C and D) for surfactant-stabilized hexane-in-water emulsions.

Acronyms of emulsions	Oil-in-water Emulsions				Droplet
	Oil		Water	Emulsifier	size
S-1	Toluene	2.5 mL	1.2 L	1.0 g/Tween 80	50 nm ~1.0 μm
S-2	Chlorof orm	3.0 mL	1.2 L	1.0 g/Tween 80	50 nm ~5.0 μm
S-3	Hexane	2.5 mL	1.2 L	1.0 g/Tween 80	100 nm ~2.0 μm

Table S1 Summarizes the acronyms of various emulsions and their composition.

Table S2 Viscosity of the oils used in oil/water separation in this work.

Oil	Density(g/cm ³)	Viscosity(mPas, 20°C)
Toluene	0.866	0.587
Chloroform	1.498	0.563
Hexane	0.659	0.307

 Table S3 Permeate flux for various emulsions of the Ag/PAA-CNTs membrane

Sample	Flux
Toluene-in-water	$2930 \pm 448 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$
Chloroform-in-water	$3220 \pm 434 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$
Hexane-in-water	$3480 \pm 555 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$

Permeate flux of the as prepared Ag/PAA-CNTs hybrid membranes: The flux of the cellulose sponge was calculated from the volume of the permeation in unit time using the following equation:

$$Flux = \frac{V}{St}$$

where V is the volume of the permeation, S is the valid area of the Ag/PAA-CNTs membrane and t is the testing time. For each test, a certain amount of emulsion (5 mL) was poured into the filter and three samples were measured to get the average value.

Supplementary movie about the as-prepared Ag/PAA-CNTs hybrid membranes: 1.Supplementary Movie S1: a water droplet on the as-prepared Ag/PAA-CNTs membrane within 5 s in air.

2.Supplementary Movie S2: an oil droplet on the as-prepared Ag/PAA-CNTs membrane within 3 s in air.

3.Supplementary Movie S3: an as-prepared Ag/PAA-CNTs membrane was obliquely placed in water, then an oil droplet was dropped on the surface of the membrane. Notice: Water was dyed with $CuSO_4$, and chloroform was dyed with oil red for a clear observation.

4.Supplementary Movie S4: an oil droplet on the as-prepared Ag/PAA-CNTs membrane under water. Notice: Water was dyed with CuSO₄, and chloroform was dyed with oil red for a clear observation.

5.Supplementary MovieS5: a Ag/PAA-CNTs membrane was applied for toluene-in-water emulsion separation .

[1]S. M. Chen, G. Z. Wu, Y. D. Liu, D. W. Long, Preparation of Poly(acrylic acid) Grafted Multiwalled Carbon Nanotubes by a Two-Step Irradiation Technique, *Macromolecules*, 2006, 39, 330-334.

[2]G. Q. Guo, F. Qin, D. Yang, C. C. Wang, H. L. Xu, S. Yang, Synthesis of Platinum Nanoparticles Supported on Poly(acrylic acid) Grafted MWNTs and Their Hydrogenation of Citral, *Chem. Mater.* 2008, 20, 2291-2297.