Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

Superwetting Polymer-decorated SWCNT Composite Ultrathin Films for Ultrafast Separation of Oil-in-Water Nanoemulsions

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1. SWCNT/PD composite films fabricated with different usage of SWCNT/PD

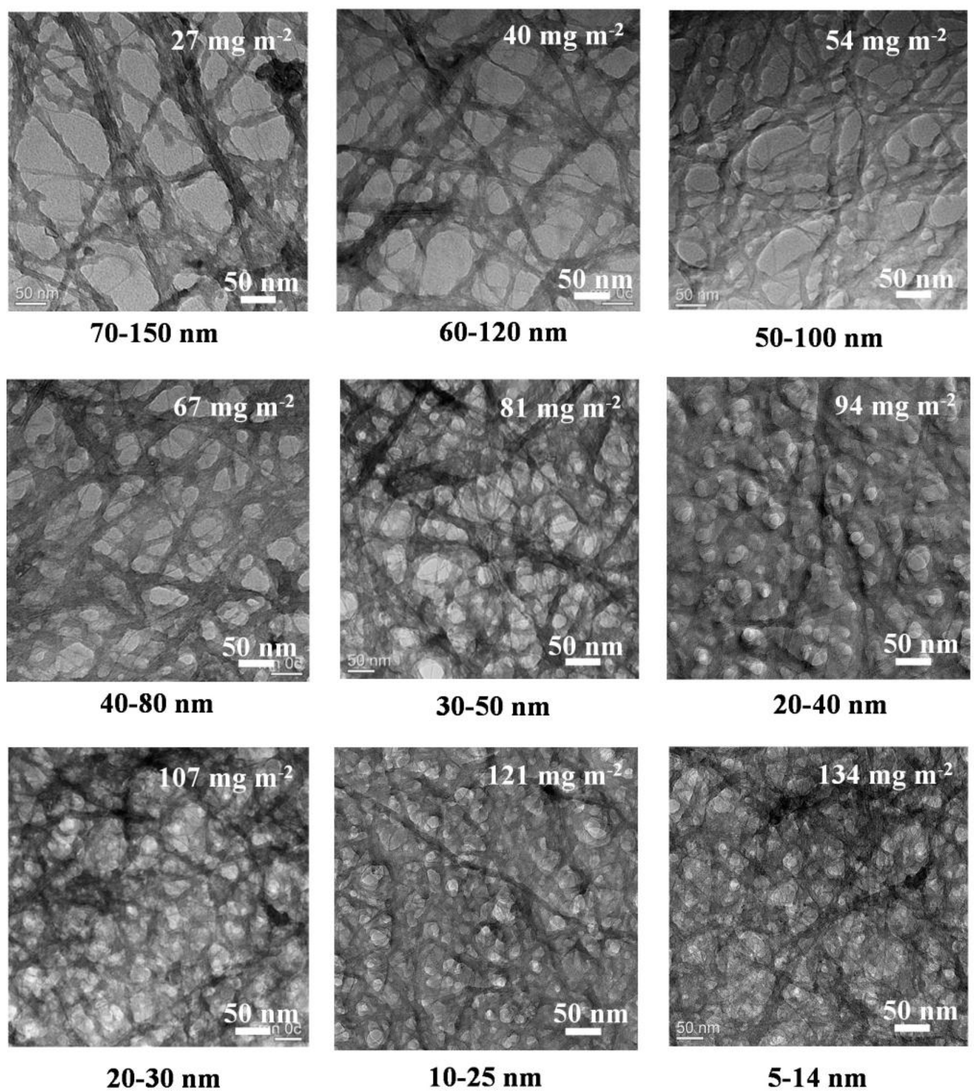

Fig. S1 TEM images and pore size of SWCNT/PD composite films with usage of SWCNT/PD of 27 mg m^{-2}, 40 mg m^{-2}, 54 mg m^{-2}, 67 mg m^{-2}, 81 mg m^{-2}, 94 mg m^{-2}, 107 mg m^{-2}, 121 mg m^{-2} and 134 mg m^{-2}, respectively.

2. Au particles rejected by the SWCNT/PD composite film

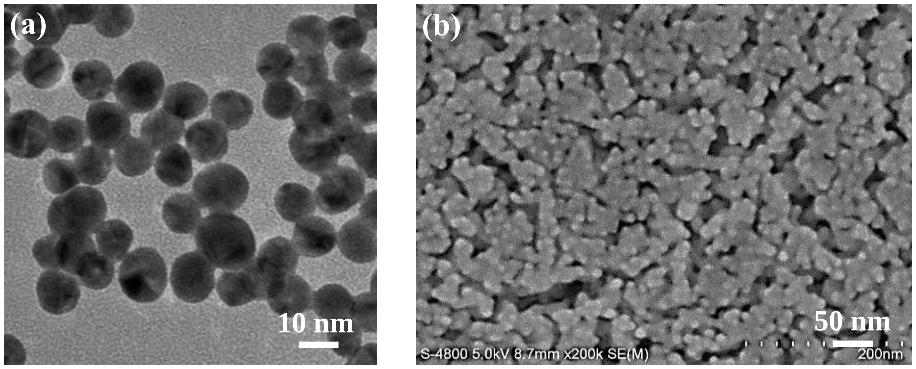

Fig. S2 (a) TEM image of the Au nanoparticle showing its size ranges from 8 nm to 14 nm. (b) SEM image showing that Au particles are rejected by the SWCNT/PD composite film rather than adsorb onto the film.

3. Underwater oil-adhesion force on the SWCNT/PD/PEI composite film

The Underwater oil-adhesion force on the SWCNT/PD/PEI composite film was dynamically measured using a 1,2-dichloroethane droplet (3 μL) as a detecting probe to contact and then leave the surface of the film under water. As shown in Fig. S3, the oil droplet was firstly forced to sufficiently touch the film with an obvious deformation, and then it was lifted up. The oil droplet didn't have any deformation when leaving the surface of the film, and no detectable oil-adhesion force was obtained during the process. This result demonstrates the underwater oil-adhesion force on the film is extremely low, simultaneously indicating the SWCNT/PD/PEI composite film behaves a superior anti-oil-fouling property.

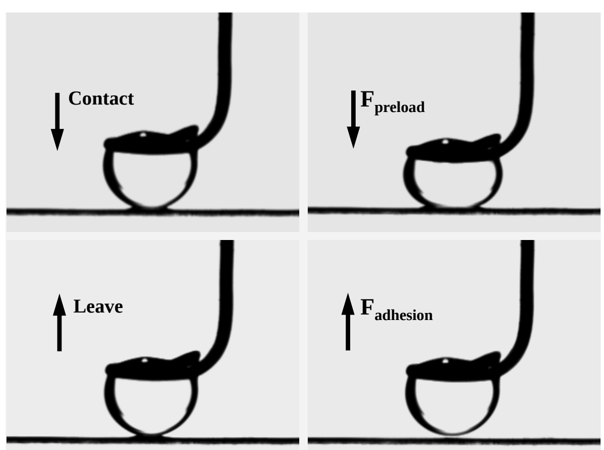

Fig. S3 Photographs of dynamic underwater oil-adhesion force measurement on the SWCNT/PD/PEI composite film. A 1,2-dichloroethane droplet was used as the detecting probe to contact (upper images) and then leave (lower images) the surface of the film.

4. Free-standing SWCNT/PD/PEI composite film showing good flexibility and strength

As shown in Fig. S4a, the free-standing SWCNT/PD/PEI composite film which is floating on the surface of a water/acetone solution can be picked up by a pipette. When the film is released, and a droplet of acetone was placed onto its surface, the film spreads out again. During the whole process, not any damage happened on the film, indicating the SWCNT/PD/PEI composite film is flexible and robust enough and could support its application for separation.

The SWCNT/PD/PEI composite film can also be successfully transferred onto other commercialized porous substrates like mesh-based, polymer-based and ceramic-based membranes. SWCNT/PD/PEI films transferred onto cupper mesh and ceramic membrane are shown below (Fig. S4b-S4c). No any damage of the film happened during the transferring process.

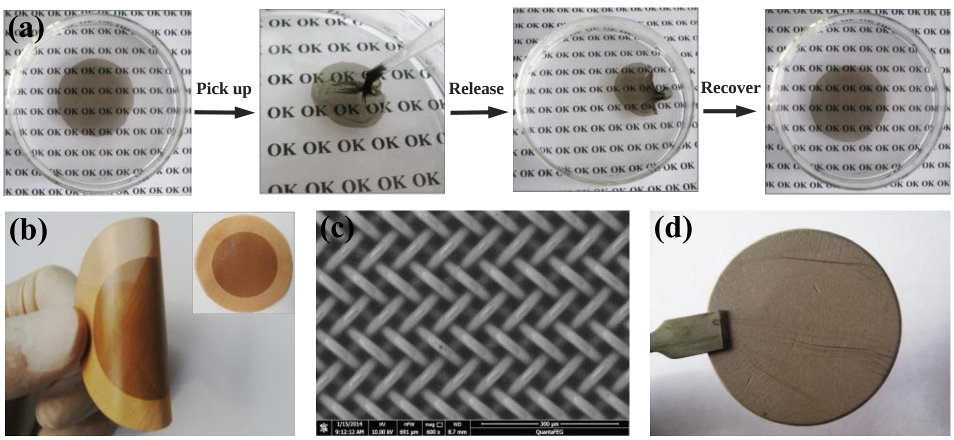

Fig. S4 (a) A cycle of picking up and releasing a free-standing SWNT/PD/PEI composite film (thickness: 158 nm) in a water/acetone solution. When a drop of acetone is placed onto the surface of the film, the film spreads out again. Optical image (b) and SEM image (c) of the SWCNT/PD/PEI film transferred onto a cupper mesh. (d) Optical image of the SWCNT/PD/PEI film transferred onto a ceramic membrane.

5. Digital photos and oil droplet size distribution of the oil-in-water nanoemulsions before and after separation.

Digital photos of the 1,2-dichloroethane-in-water nanoemulsion and industrial oil-in-water nanoemulsion before and after separation by the SWCNT/PD/PEI composite film are shown in Fig. S5 (left images). The transparent emulsion feeds have obvious Tyndall effects if illuminated by a 650 nm laser, indicating there are massive oil droplets with size below 100 nm in the emulsion feeds. But in the filtrates, no Tyndall effects are observed if illuminated by the same laser. This result demonstrates the nano-sized oils have been successfully removed and the excellent separation efficiency of the SWCNT/PD/PEI composite film for oil-in-water nanoemulsions with oil droplets of tens of nanometer.

Oil droplet size distribution of these oil-in-water nanoemulsions in feed and filtrate was also examined by DLS measurement. As shown in Fig. S5 (right graph), the oil droplet size of the dichloroethane-in-water emulsion feed and industrial oil-in-water emulsion feed are mainly distributed around 52 nm and 61 nm. After separation, no oil droplets around these ranges are observed, indicating the high separation efficiency of the SWCNT/PD/PEI composite film.

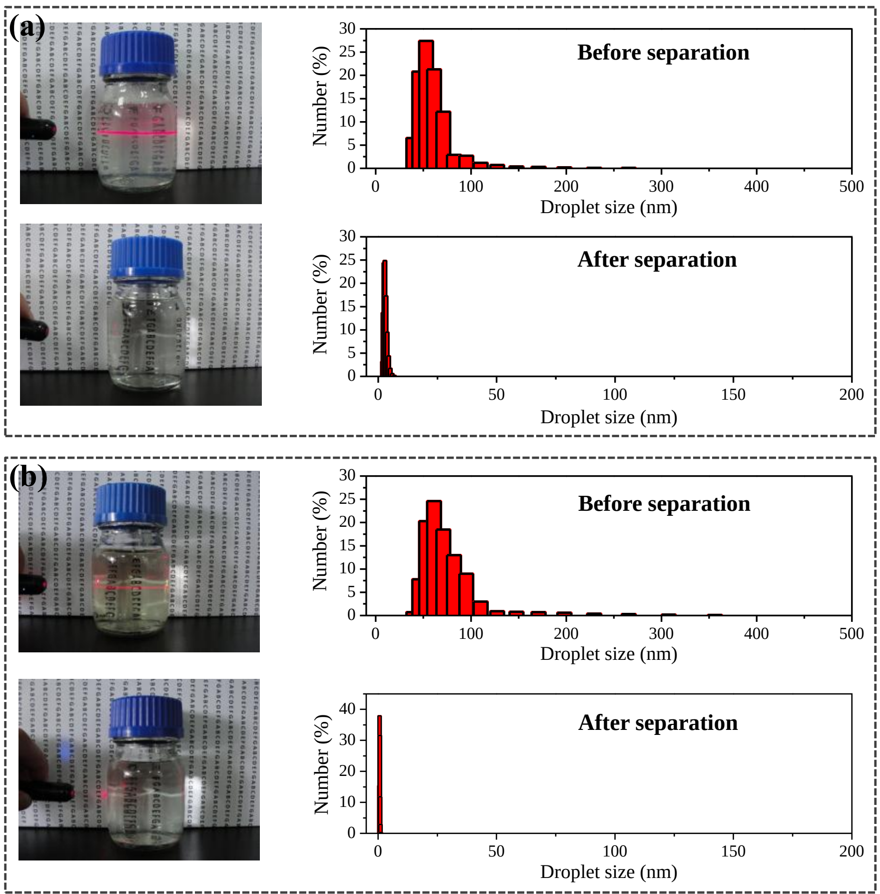

Fig. S5 Digital photos (left) and oil droplet size distribution (right) of the 1,2-dichloroethane-in-water nanoemulsion (a) and the industrial oil-in-water nanoemulsion (b) before and after separation by a 158-nm-thick SWCNT/PD/PEI composite film.

6. Table S1 Summary of the SWCNT/PD/PEI composite film and its separation performance for oil-in-water nanoemulsions

	Characterization of the film			
	Usage of SWCNT/PD (mg/m^2)	Average film thickness (nm)	Pore size (nm)	Pure water flux ($L\ m^{-2}h^{-1}bar^{-1}$)
SWCNT/PD film	27	31±3	70-150	38800±2200
	40	42±4	60-120	29200±1800
	54	55±5	50-100	24000±1900
	67	68±5	40-80	20400±1600
	81	87±6	30-50	16300±1500
	94	104±5	20-40	14200±1200
	107	123±5	20-30	11000±900
	121	141±6	10-25	9200±700
	134	154±5	5-14	8100±700
SWCNT/PD/PEI film	134	158±6	5-14	7270±600

	Separation performance						
	Nanoemulsion	Average oil droplet size (nm)		Oil content including surfactant (ppm)		Water purity after separation (%)	Permeation flux ($L\ m^{-2}h^{-1}bar^{-1}$)
		Before separation	After separation	Before separation	After Separation		
SWCNT/PD/PEI film	Isooctane-in-water	54±5	2.2±0.7	2090	28.1±3.1	99.997	3030±220
	Dichloroethane-in-water	52±4	2.8±0.9	13000	33.4±3.3	99.997	3390±190
	Industrial oil-in-water	61±6	0.7±0.2	1230	27.8±2.5	99.997	6060±350

7. Table S2 Comparison between SWCNT/PD/PEI film and other oil/water separation membranes for oil-in-water emulsions with nano-sized oils.

Membranes	Oil droplet size in the oil-in-water emulsion	Separation flux ($L\ m^{-2}h^{-1}bar^{-1}$)	Oil rejection rate (%)	Reference
SWCNT/PD/PEI film	50-70 nm	3030-6000	97.7-99.7	This paper
Cellulose nanosheet membrane	80-200 nm	1150-1590	96.7-98	Ref. 1
Intelligent superwetting PVDF membrane	40-60 nm	2580-9380	Not shown in original paper	Ref. 2
Al_2O_3/TiO_2 modified PVDF UF membrane	100–600 nm	157	Not shown in original paper	Ref. 3

References:

1. K. Zhou, Q. G. Zhang, H. M. Li, N. N. Guo, A. M. Zhu, Q. L. Liu, *Nanoscale*, 2014, **6**, 10363-10369.

2. M. Tao, L. Xue, F. Liu, L. Jiang, *Adv. Mater.*, 2014, **26**, 2943-2948.
3. X. S. Yi, S. L. Yu, W. X. Shi, S. Wang, N. Sun, L. M. Jin, C. Ma, *Desalination*, 2013, **319**, 38-46.