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Supporting Information *for*

Controlled Functionalization of Carbon Nanotubes as Superhydrophobic Materials for Adjustable Oil/Water Separation

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Materials: General chemicals in chemical reagent grade were used as received from Sinopharm Chemical Reagent.1H, 1H, 2H, 2H-Perfluorodecyltriethoxysilane (PFDTS) was obtained from Alfa Aesar China (Tianjin) Co., Ltd. The raw multi-wall carbon nanotubes (CNTs, diameter about 10-30 nm and length about 10-30 μm, -OH % about 2%) with a purity of over 90% was purchased from Chengdu Organic Chemistry Co., Ltd, which was rinsed thoroughly with anhydrous ethanol, dried in a stream of nitrogen before use. Poly (vinylidene fluoride) (PVDF) membrane was purchased from Sea Peninsula Industrial Co., Ltd.

Preparation of PFDTS/CNTs hybrid membranes: 40 mg purified CNTs was dispersed in 20 mL toluene and sonicated for 30 min.1 mL PFDTS was dispersed in 19 mL toluene and sonicated for 30 min. A certain volume of PFDTS/toluene was added to the CNTs/toluene, the volume ratio of PFDTS to CNTs was 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, respectively. The mixture was sonicated for another 30 min. 10 mL mixture solution was then filtrated on the PVDF membrane with the vacuum degree at 0.09 MPa to form PFDTS/CNTs hybrid membrane.

Preparation of the Water-in-Oil Emulsions: 0.6 g of span80 (HLB = 4.3, an emulsifier of the water-in-oil type) was added into 114 mL oil, and then 1 mL water was also added. The mixture was stirred for 3 h. All the prepared emulsions were stable for 24 h and no demulsification was observed. The composition of various emulsions is summarized in Table

S2. The density and viscosity of all the oils used in this work are summarized in Table S4.

Separation of Water-in-Oil emulsions: The separation experiments were carried out with a vacuum driven filtration system with the vacuum degree at 0.09 MPa. The diameter of the filter is 4 ± 0.1 cm.

Characterizations: Static water contact angles (WCA) measurements were measured at room temperature using an OCA-20, dataphysics instrument. The water (Milli-Q) droplet volume was 3 μL, and average of three measurements was made to determine the surface wettability. Transmission electronic microscopy (TEM) measurements were performed with a JEOL JEM-2100F microscope. Scanning electronic microscopy (SEM) measurements were carried out using a JEOL JMS-6700F scanning microscope. XPS analysis was performed on a Shimadzu Axis Ultradld spectroscope, using Mg-K (alpha) as radiation resource. Optical microscopy images were taken on BX 51TF Instec H601. Dynamic light scattering (DLS) measurement was performed on a Zetasizer Nano ZS. The water contents in collected filtrates were determined using a Karl Fischer moisture titrator (KF831).

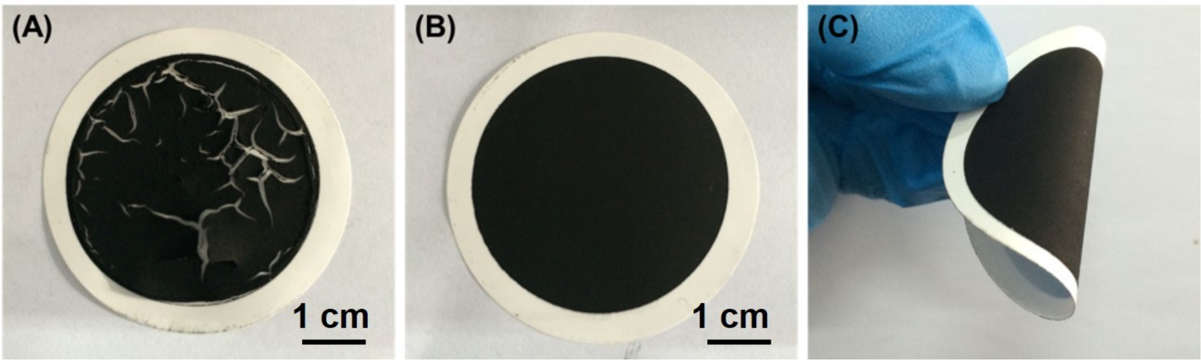

Fig. S1 Photographs of (A) a CNTs membrane on PVDF membrane substrate, (B) a PFDTS/CNTs membrane on PVDF membrane substrate, (C) a bended PFDTS/CNTs membrane. Notice: from Fig. S1B to S1C, the volume ratio of PFDTS and CNTs is 1.25.

PFDTS/CNTs membranes with different PFDTS/CNTs ratio were prepared. As shown in **Fig. S2** and **S3**, the average diameter of PFDTS/CNTs increases with increasing ratio of PFDTS/CNTs. The water contact angle also increases with increasing ratio of PFDTS/CNTs, and finally reaches a constant level (**Fig. S4**). At ratio 1.25, the PFDTS/CNTs membrane already shows superhydrophobic property, therefore, this ratio was chosen for water/oil separating experiment.

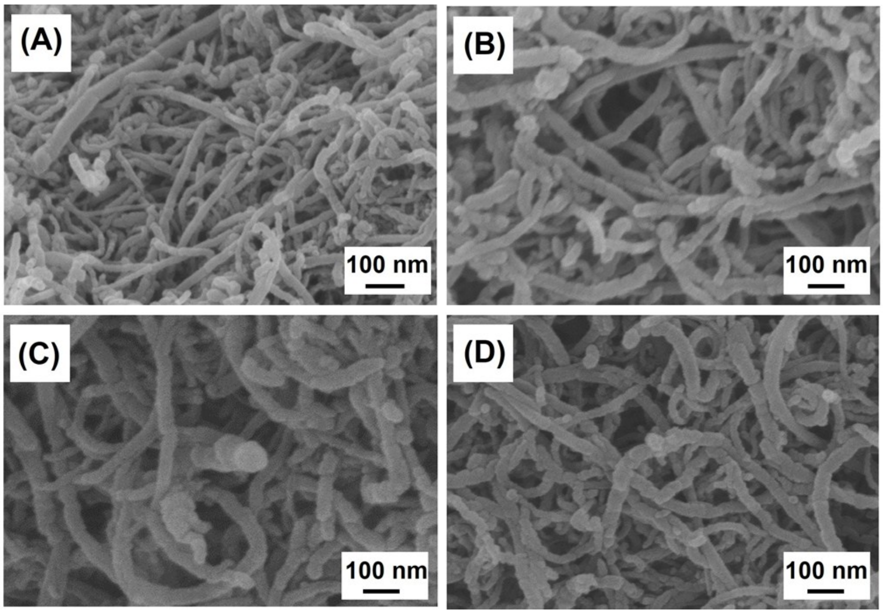

Fig. S2 SEM images of PFDTS/CNTs membrane with the volume ratio of PFDTS/CNTs (A) 0.75, (B) 1.00, (C) 1.50, (D) 1.75.

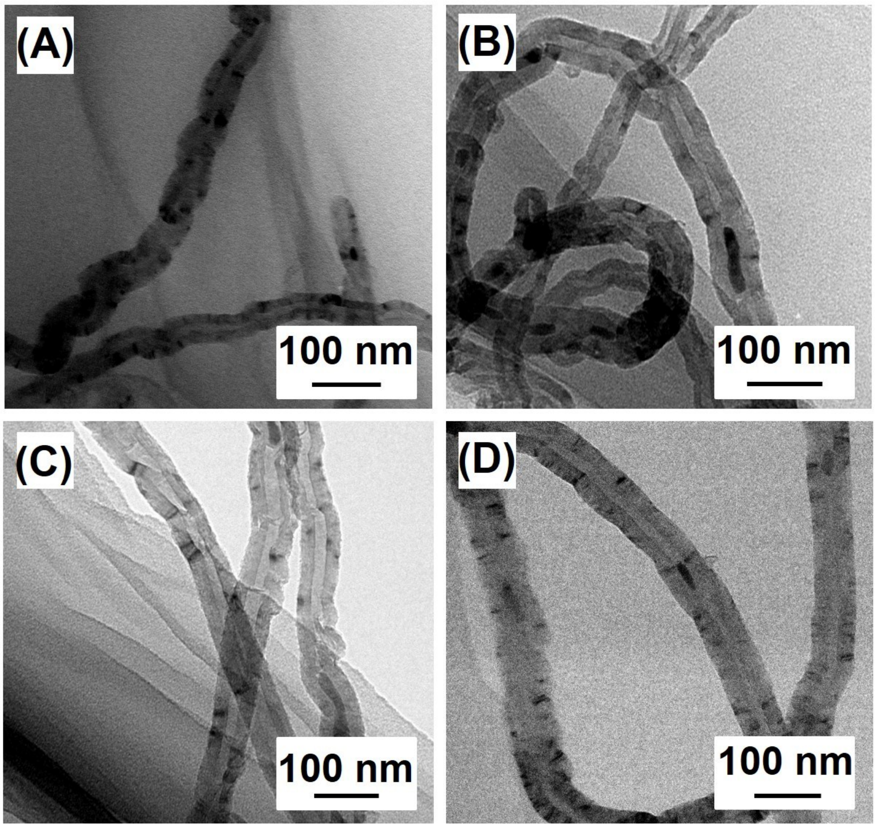

Fig. S3 TEM images of PFDTS/CNTs membrane with the volume ratio of PFDTS/CNTs (A) 0.75, (B) 1.00, (C) 1.50, (D) 1.75.

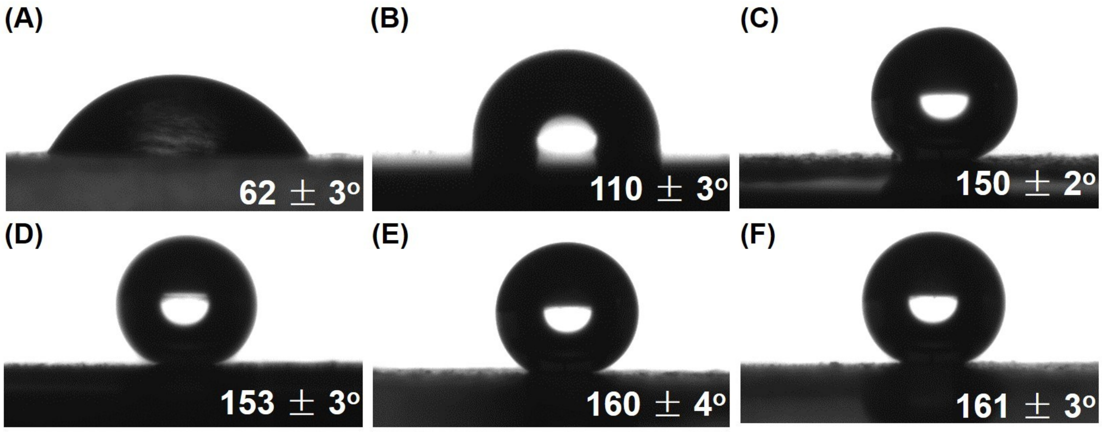

Fig. S4 Static WCA measurements for (A) CNTs membrane , PFDTS/CNTs membrane with the volume ratio of PFDTS/CNTs at (B) 0.50, (C) 0.75, (D) 1.0 (E) 1.25, (F) 1.50.

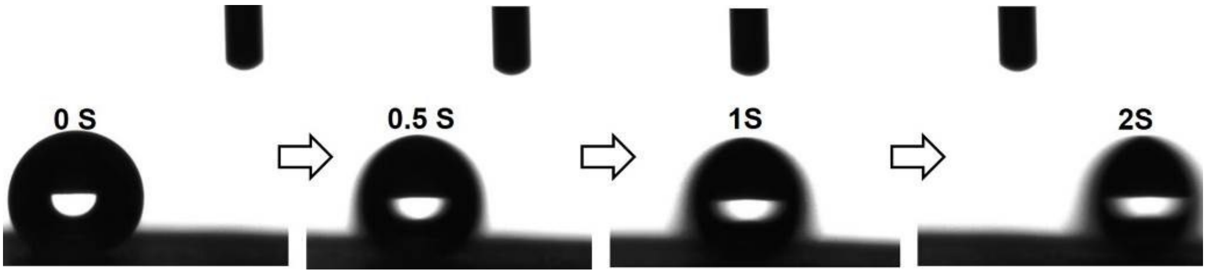

Fig. S5 Photographs of a water droplet (3 μL) sliding at a low angle of sliding on the surface of as-prepared PFDTS/CNTs membrane with an angle of 3.0 ± 0.6° on the surface of as-prepared PFDTS/ CNTs membrane. Notice: the volume ratio of PFDTS to CNTs is 1.25.

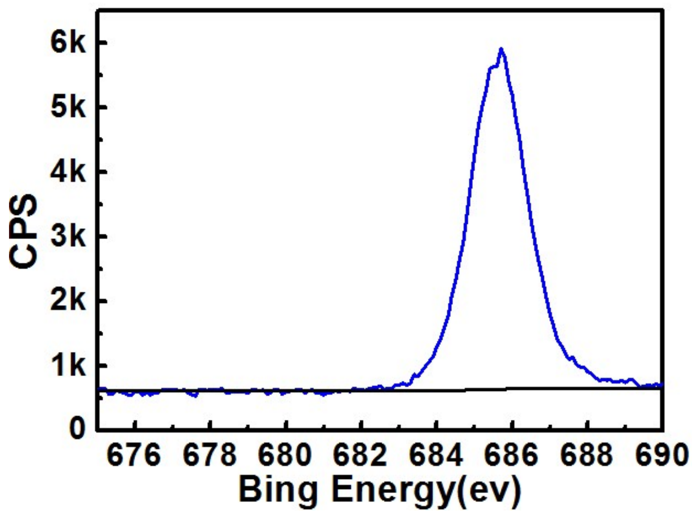

Fig. S6 XPS spectra of F 1s spectrum of PFDTS/CNTs membrane. Notice: the volume ratio of PFDTS and CNTs is 1.25.

Table S1 Element concentration as determined by XPS analysis.

	XPS Mass Concentration Concentration(%)			
	C	O	F	Si
CNTs	96.77	3.23	—	—
PFDTS/CNTs	72.25	3.03	23.04	1.68

If there was no PFDTS/CNTs, the PVDF membrane also shows hydrophobicity **(Fig. S7)**. However, the PVDF membrane cannot separate oil/water mixtures (**Fig. S8C** and **Movie S3**). The PFDTS/CNTs membrane can effectively separate oil/water mixtures (**Fig. S8B** and **Movie S4**), indicating PVDF membrane just act as a substrate to the PFDTS/CNTs membrane, and the oil/water separation performance is exhibited by the PFDTS/CNTs membrane.

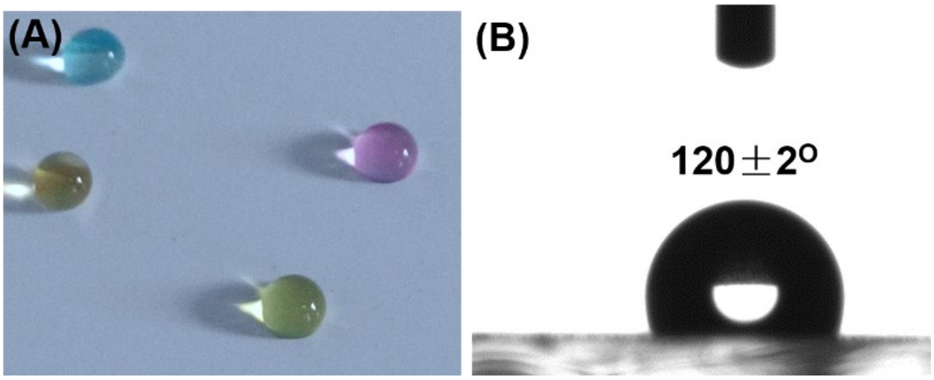

Fig. S7 (A) A PVDF membrane with water droplets (water was dyed with $KMnO_4$, $CuSO_4$, and $FeCl_3$, $K_2Cr_2O_7$, respectively). (B) The WCA of the PVDF membrane.

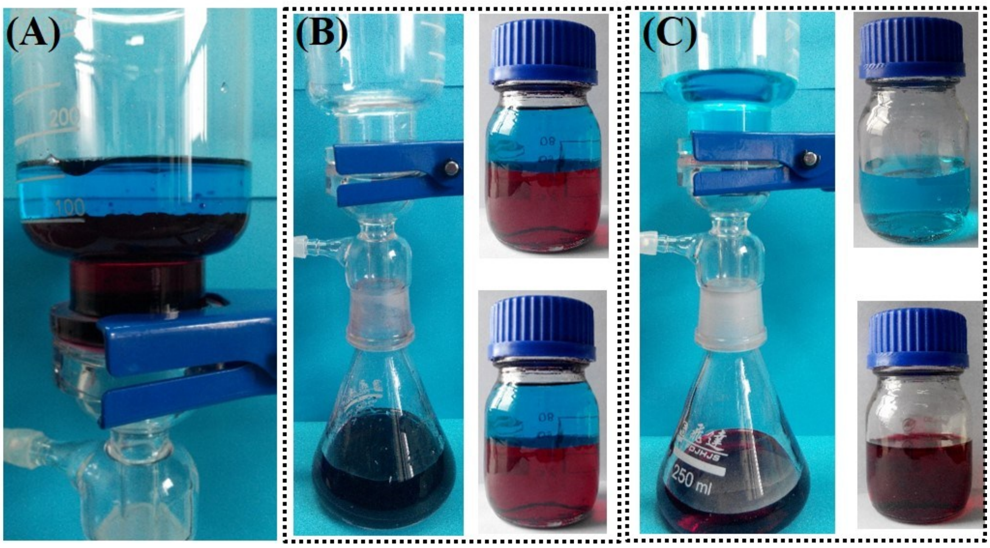

Fig.S8 (A) Photograph of chloroform/water mixture before separation, (B) PVDF membrane was applied for chloroform/water separation, (C) Superhydrophobic PFDTS/CNTs membrane was applied for chloroform /water separation. Water was dyed with $CuSO_4$, and chloroform was dyed with oil red for a clear observation.

The emulsion droplets before and after filtration were monitored by DLS (**Fig. S9**). The droplet size distribution for water-in-chloroform and water-in-hexane emulsions are around 150 nm, 200 nm, respectively. After filtration, no droplets around these ranges are observed.

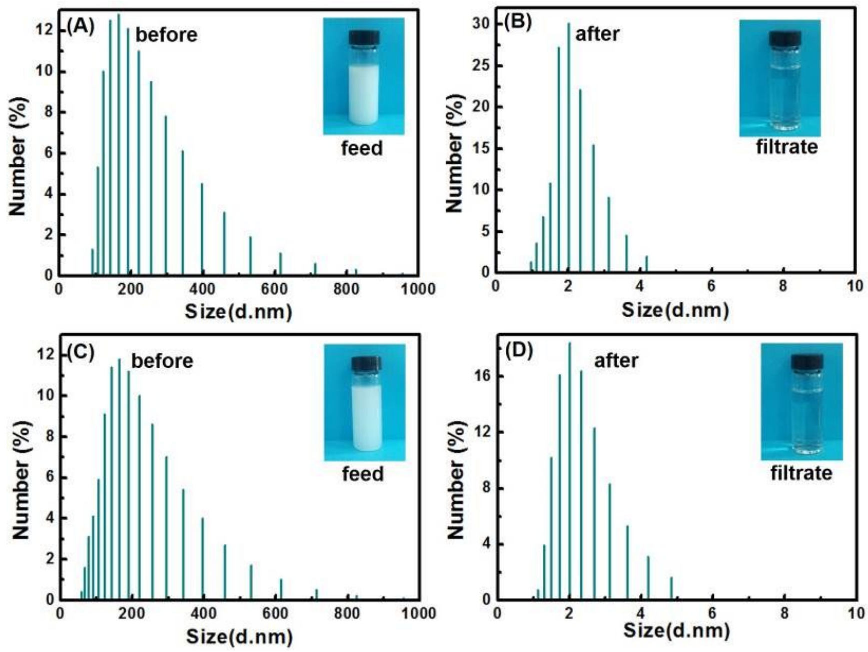

Fig. S9 DLS data of the feed emulsions (up) and their filtrate correspondingly (down) for surfactant-stabilized emulsions of S-2 (water-in-chloroform, A-B) and S-3 (water-in-hexane, C-D). Notice: the volume ratio of PFDTS to CNTs is 1.25.

Optical microscopy images of surfactant-stabilized emulsions before and after filtration are shown in **Fig. S10**. Emulsion droplets in micrometer size are clearly observed in feed solution. However, droplets are not observed in collected filtrate in the whole view, indicating the effective separation.

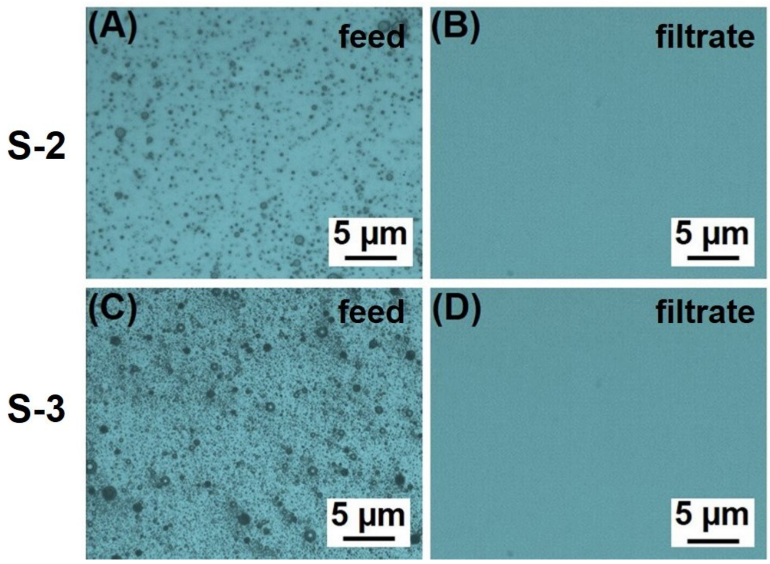

Fig. S10 Optical microscopy images of the feed emulsions and their filtrate correspondingly for surfactant-stabilized emulsions of S-2(water-in-chloroform, A-B) and S-3(water-in-hexane, C-D). Notice: the volume ratio of PFDTS to CNTs is 1.25.

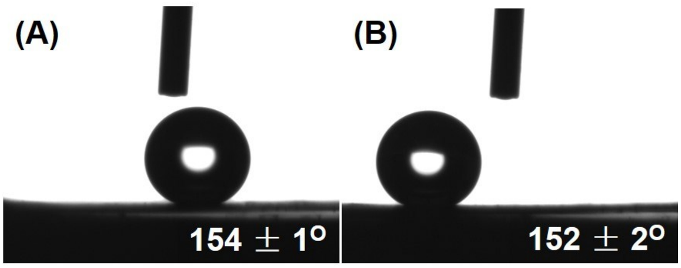

Fig. S11 Static WCA measurements for PFDTS/CNTs membrane (A) before burning, (B) after burning.

Table S2 Summarizes the acronyms of various emulsions and their composition.

	Emulsion		
	Oil	Water	Emulsifier
S-1	Toluene 114 ml	1 ml	0.6 g/Span 80
S-2	Chloroform114 ml	1 ml	0.6 g/Span 80
S-3	Hexane 114 ml	1 ml	0.6 g/Span 80

Table S3 Oil purity of filtrate.

	S-1	S-2	S-3
Oil purity of the filtrate	99.89%	99.91%	99.93%

Table S4 Viscosity of the oils used in oil/water separation in this work.

	Viscosity (mPa,20°C)		
	Toluene	Chloroform	Hexane
Oil	0.587	0.563	0.307

Calculation of fluxes of PFDTS/CNTs membrane

The flux of PFDTS/CNTs membrane was determined by calculating the volume of permeate in unit time by using the following equation:

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

Where V is the volume of the permeated emulsion, S is the valid area of the PFDTS/CNTs membrane and t is the testing time.

Supplementary movie about the as-prepared PFDTS/CNTs membrane

1. **Supplementary Movie S1:** the macro characterization of the superhydrophobicity of the as-prepared PFDTS/CNTs membrane when the volume ratio of the PFDTS/CNTs is 1.25.
2. **Supplementary MovieS2:** a water droplet on the as-prepared membrane with a sliding angle of 3.0±0.6°.
3. **Supplementary MovieS3:** a PVDF membrane was applied for chloroform/water separation. Water was dyed with $CuSO_4$, and chloroform was dyed with oil red for a clear observation.
4. **Supplementary MovieS4:** a PFDTS/CNTs membrane was applied for chloroform/water separation when the volume ratio of the PFDTS/CNTs is 1.25. Water was dyed with $CuSO_4$, and chloroform was dyed with oil red for a clear observation.
5. **Supplementary MovieS5:** a PFDTS/CNTs membrane was applied for water-in-toluene emulsion separation when the volume ratio of the PFDTS/CNTs is 1.25.
6. **Supplementary MovieS6:** the combustion behavior of the as-prepared PFDTS/CNTs membrane when the volume ratio of the PFDTS/CNTs is 1.25.