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Robust Preparation of Superhydrophobic Polymer/Carbon Nanotube Hybrid Membranes for Highly Effective Removal of Oils and Separation of Water-in-Oil Emulsions

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Materials: General chemicals in chemical reagent grade were used as received from Sinopharm Chemical Reagent. Toluene, ethyl acetate, ethanol and deionized water were used as rinsing solvents. Styrene (99%) was obtained from Alfa Aesar China (Tianjin) Co., Ltd, which was purified by neutral Al_2O_3 column and dried with 0.4nm molecular sieve at room temperature for 3 days. The raw CNTs (diameter about 10-30 nm and length about 30 μm) 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. Solid Al_2O_3 membrane substrates were cleaned in a mixture of NaOH (0.1 M) and ethanol (1:2, v:v) at 25 ^{o}C for 2 h and washed thoroughly with Mill-Q-grade water.

Self-initiated photografting and photopolymerization (SIPGP): It was demonstrated that polymer brushes can be prepared even without a surface-bound initiator by SIPGP [1~3]. The SIPGP allows us to have a robust choice due to its several advantages including no additional surface analog reaction to introduce a photo-initiator and very stable covalent attachment of the polymer brush to the surface via C–C bonds. The mechanism of the auto-initiated polymerization of styrene monomer under UV radiation has been briefly outlined in previous report[1].

Preparation of superhydrophobic Polymer/CNTs Hybrid membranes: Superhydrophobic polymer/CNTs hybrid membranes were synthesized by self-initiated photografting and photopolymerization (SIPGP). Briefly, 2 mg purified CNTs was dispersed in 1 mL ethanol and sonicated for 3 h, the mixture was then dropped uniformly on the Al_2O_3 membrane substrates. After drying, the membrane was submerged in a glass tube containing degassed styrene monomer, and irradiated with an UV fluorescent lamp with a spectral distribution between 300 and 400 nm (intensity maximum at $\lambda = 350$ nm with a total power of ~210 mW/cm^2) under nitrogen atmosphere for 30 min. After self-initiated photografting and photopolymerization (SIPGP), each as-prepared PS-g-CNTs membrane was rigorously rinsed with toluene, ethyl acetate and ethanol to remove the physisorbed polymer and monomer.

Sorption of organic solvents: Firstly, 4 mg oil red (an organic dye, the organic solvent can be dyed red with oil red) was added in 15 mL n-hexane, the mixture was sonicated for 10 min to form a homogeneous solution. Secondly, 1 mL n-hexane dyed with oil red was added to water surface. The oil droplet was in the upper layer of water because of lower density, which can form a homogeneous oil layer. Lastly, a PS-g-CNTs hybrid membrane was placed in contact with n-hexane dyed with oil red until the n-hexane was completely absorbed by the membrane. In this process, the PS side of the PS-g-CNTs hybrid membrane was on the upper side, and the side without PS was in contact with water.

The sorption of other organic solvents was performed by the same procedure. We should emphasize that the test should be done quickly in order to avoid evaporation of the absorbed organic solvents, especially for those with low boiling points.

Separation of water-in-oil emulsions: Three kinds of surfactant-stabilized water-in-oil emulsions labeled as S1 for water/toluene emulsion, S2 for water/hexadecane emulsion and S3 for water/dichloromethane emulsion were prepared. The procedure is as follows: For S1and S3, span80 (1.5 g) was added into oil (1.2 L), and then water (10 mL) was added, for S2 span80 (3.0 g) was added into oil (1.2 L), and then water (10 mL) was added. The mixture was stirred for 3 h to obtain surfactant-stabilized emulsions, and all the emulsions were stable for more than 2 weeks without demulsification or precipitation was observed. The separation was carried out by using a filter with a diameter of 25 mm. Dispersed emulsions were poured into the filtration cell and were suction filtered under a pressure of 10 kPa.

Characterizations: 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 equipped with an energy-dispersive X-ray (EDX) Oxford ISIS 300 micro analytical system. Fourier transform infrared (FTIR) spectra were performed on a Varian Scimitar1000 Fourier transform IR spectrophotometer. TGA measurements were conducted with a Netzsch TG 209F1 instrument with a heating rate of 10 °C/min under N_2 atmosphere. The Raman measurements were recorded on a Dilor LabRam-1B multi-channel confocal microspectrometer with 532 nm laser excitation. 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 were made to determine the surface wettability. Optical microscopy images were taken on Nikon AZ100 by dropping emulsion solution on biological counting board. The water contents in collected filtrates were determined using a Karl Fischer moisture titrator (KF831). Dynamic light scattering (DLS) measurement was performed on a Zetasizer Nano ZS.

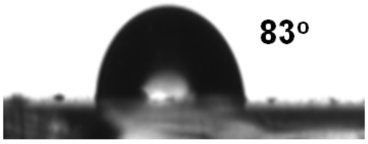

Fig. S1 Static WCA for CNTs membrane after 30min UV irradiation.

The attachment of PS was also confirmed by FTIR and Raman results. As shown in Fig. S2A, the absorption peak at 3450 cm^{-1}and 1633 cm^{-1} in the FTIR spectrum of CNTs corresponded to the characteristic -OH bonds stretching vibrations and C=C bonds stretching vibrations, respectively. [4] After SIPGP, new bands at 3029 cm^{-1} and 2934 cm^{-1}, which are contributed by -CH- and -CH_2- stretching vibration of PS, are observed. Fig. S2B displays the Raman spectra of CNTs and PS-g-CNTs membranes. The CNTs membrane shows the significant characteristic spectrum of the D and G mode with I_D/I_G of 0.87. After modification of PS, the I_D/I_G ratio of PS-g-CNTs apparently increases to 0.97 (Fig. S2C), indicating the covalent side-wall functionalization of CNTs. [4] In addition, compare with

CNTs, red shift of the D, G and G′ bands of PS-g-CNTs is observed, which are attributed to the weaker mutual electronic interaction between CNTs after modification. [5, 6] Both the FTIR and Raman results provide direct evidence of the successful covalent attachment of PS brushes to the CNTs membrane.

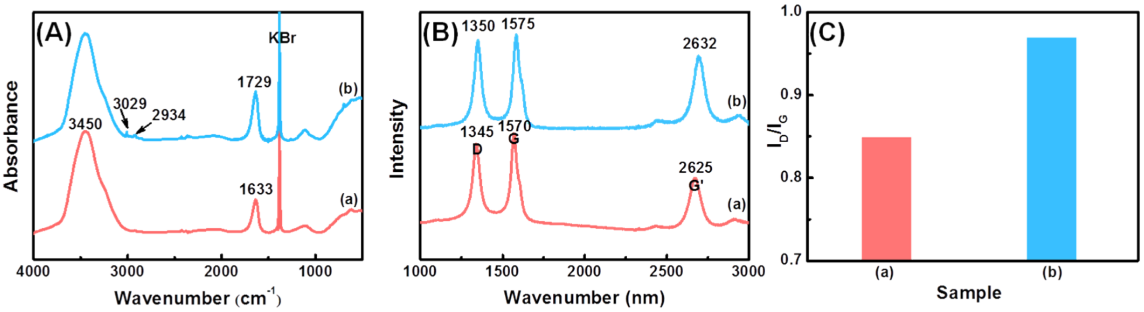

Fig. S2 (A) FT-IR spectra of (a) CNTs, (b) PS-g-CNTs. (B) Raman spectra of (a) CNTs, (b) PS-g-CNTs. (C) Values of I_D/I_G (a) CNTs, (b) PS-g-CNTs.

The grafting of PS from CNTs membrane was also determined by TGA. As shown in Fig. S3, PS is almost completely decomposed at around 450 °C, and the weight loss of PS-g-CNTs at 450 °C is about 70%, indicating PS is grafted from the surface of CNTs. The relative amount of grafted PS on CNTs is estimated to be 20% (Fig. S3).

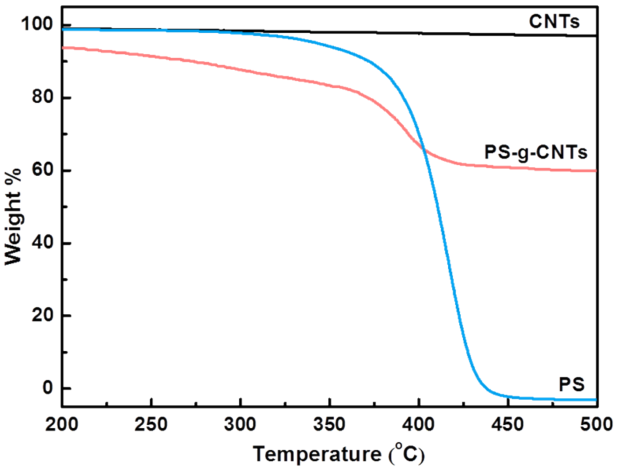

Fig. S3 TGA curves of CNTs, PS and PS-g-CNTs.

Droplet size distribution of surfactant-stabilized emulsions in feed and filtrate

Optical microscopy images of surfactant-stabilized emulsions before and after filtration are shown in Figure S4. 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.

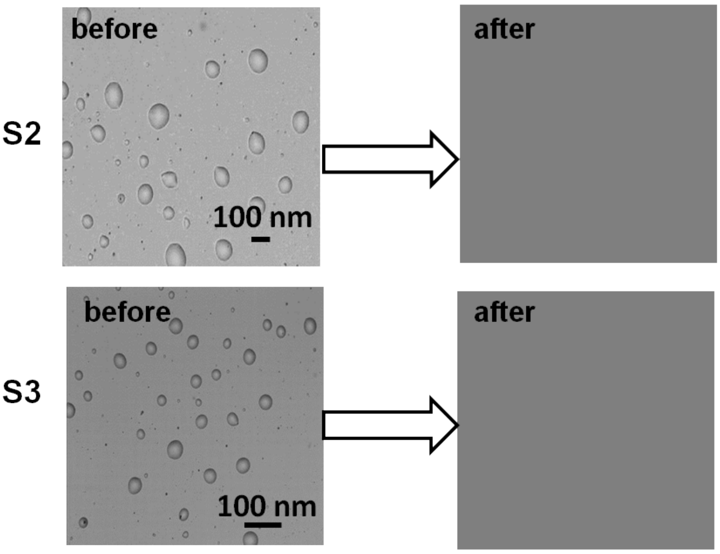

Fig. S4 Optical microscopy images of the feed emulsions (up) and their filtrate correspondingly (down) for surfactant-stabilized emulsions of S2 (water/dichloromethane/span80) and S3 (water/hexadecane /span80).

The emulsion droplets before and after filtration were monitored by DLS. The droplet size distribution for water/toluene/span80, water/dichloromethane/span80 and water/hexadecane/span80 emulsions are around 70 nm, 170 nm and 60 nm, respectively. After filtration, no droplets around these ranges are observed. Note: the sharp peak appearing at 1 nm is an unavoidable error signal during DLS testing for a pure liquid.

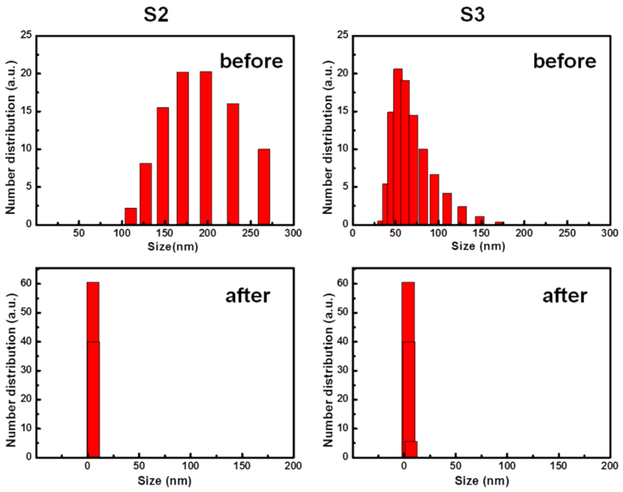

Fig. S5 DLS data of the feed emulsions (up) and their filtrate correspondingly (down) for surfactant-stabilized emulsions of S2 (water/hexadecane/span80) and S3 (water/dichloromethane /span80).

Calculation of fluxes of PS-g-CNTs membrane

The flux of PS-g-CNTs membrane was determined by calculating the volume of permeate in unit time by using the following equation:

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

Where V is the volume of the permeated emulsion, S is the valid area of the PS-g-CNTs membrane and t is the testing time. The flux was determined within 5 min for each sample.

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