Photoinduced Superwetting Single-Walled Carbon Nanotube/TiO_2 Ultrathin Network Films for Ultrafast Separation of Oil-in-Water Emulsions

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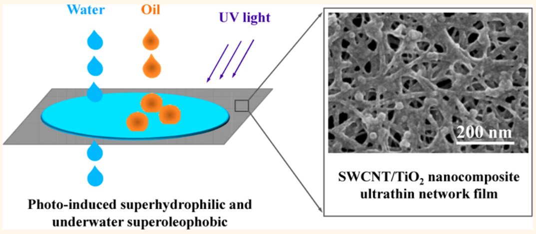
ABSTRACT A SWCNT/TiO_2 nanocomposite ultrathin film that has superhydrophilic and underwater superoleophobic properties after UV-light irradiation is successfully prepared by coating TiO_2 *via* the sol–gel process onto an SWCNT ultrathin network film. The robust and flexible SWCNT/TiO_2 nanocomposite films with a thickness and pore size of tens of nanometers can separate both surfactant-free and surfactant-stabilized oil-in-water emulsions in an ultrafast manner with fluxes up to 30 000 L m^{-2} h^{-1} bar^{-1}, which is 2 orders of magnitude higher than commercial filtration membranes with similar separation performance, and with high separation efficiency. Most importantly, the films exhibit excellent antifouling and self-cleaning performance during multiple cycles with the aid of the photocatalytic property of TiO_2 nanoparticles. This work provides a route for designing ultrathin and superwetting films for effective separation of oil-in-water emulsions. The SWCNT/TiO_2 ultrathin film is potentially useful in treating emulsified wastewater produced in industry and daily life and for purification of crude oil and fuel.



KEYWORDS: emulsion separation · superhydrophilic and underwater superoleophobic · SWCNT/TiO_2 nanocomposite film · ultrathin film

Emulsified oil in wastewater is a major environmental issue affecting a range of industries. Direct discharge of the wastewater will harm the environment and people's health.[1,2] This issue is more serious for the wastewater from an oil-in-water emulsion than that from other types of oil/water mixtures in view of how to treat the oil/water mixture. Removing emulsified oil from wastewater is always a job that is tough and challenging.[3] The current technology for wastewater treatment is to use a polymer or ceramic filtration membrane, which is regarded as a better technology than other techniques from an operational point of view, especially for surfactant-stabilized oil-in-water emulsions to meet discharge standards and with a simple process.[4−11] However, polymer- or ceramic-based membrane technology has drawbacks including low flux, fouling, and quick decline of efficiency due to surfactant adsorption and/or pore plugging by oil droplets, which give rise to high costs for treating large effluent volumes.[12−17] It is highly demanded to design and develop new more advanced filtration membranes to replace polymer and ceramic membrane technology to effectively remove emulsified oil from various wastewater.

A classical fluid dynamic theory is the Hagen–Poiseuille equation:

$$J = \varepsilon \pi {r_p}^2 \Delta p / 8 \mu L \qquad (1)$$

where the flux J is described as a function of the surface porosity ε, the membrane pore radius r_p, the pressure drop Δp,the viscosity of the liquid μ, and the total distance L of the liquid running through the membrane. The fluid dynamic theory predicts that the filtration rate is directly proportional to the square of the effective pore size and inversely proportional to the thickness of the membrane.[18,19] It indicates that good design of membranes for removing emulsified oil from wastewater requires optimizing these two parameters. An ideal filtration membrane is one that is as thin as possible

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and does not sacrifice its effective pore size.[20,21] However, it is hard to achieve this in a filtration system made from polymeric or ceramic membranes. Recently, good progress on oil/water separation has been made on the development of superwetting materials that have either a superhydrophobic−superoleophilic surface or a superhydrophilic−superoleophobic surface.[22−29] However, most of them are coated with hydrophobic or hydrophilic materials on a mesh-like matrix with a pore size at the micrometer scale. Few of them are applicable for the separation of emulsified oil/water mixtures in a wide range of droplet size from micrometer to nanometer.[22−24,30−32]

Most recently, we reported a new technology for the design and development of an ultrathin film of single-walled carbon nanotubes (SWCNTs) that could effectively separate emulsified oil from oil/water mixtures with ultrahigh flux and high separation efficiency.[33] However, the technology is good for separation of oil-rich mixtures, such as water-in-oil emulsions, but does not work for oil-in-water emulsions due to hydrophobic and superoleophilic surface wetting properties of the SWCNT film. To achieve the latter goal, it would be essential to design and develop a filtration membrane that is superhydrophilic and underwater superoleophobic, an idea that is inspired by the antiwetting behavior of oil droplets on fish scales in water.[34−36] Combining the photoresponsive wettability of TiO_2,[37−41] we developed an ultrathin film made of an SWCNT network and TiO_2 nanocomposite, which posesses superhydrophilic and underwater superoleophobic properties. This is materialized by employing UV-light irradiation. The SWCNT ultrathin network film provides a unique structure down to nanoscale thick with nanoscale pore size, which is much better than traditional filtration membranes and mesh-based superwetting films for oil/water separation.[14,22,29−32] Our SWCNT/TiO_2 nanocomposite film, which is tens of nanometers thick, can separate both a surfactant-free emulsion and a surfactant-stabilized oil-in-water emulsion with very high flux, up to 30 000 L m^{-2} h^{-1} bar^{-1}. This figure is 2 orders of magnitude higher than commercial filtration membranes and with a high separation efficiency (oil content after treatment is <40 ppm, meeting the standards for wastewater discharge). Most importantly, the SWCNT/TiO_2 nanocomposite film exhibits excellent antifouling properties and self-cleaning during multiple cycles with the aid of TiO_2 nanoparticles, which are photocatalytic.

RESULTS AND DISCUSSION

Preparation and Morphology Characterization of SWCNT/TiO_2 Nanocomposite Film. The SWCNT/TiO_2 nanocomposite film was prepared by coating TiO_2 *via* the sol−gel process onto an SWCNT network film, as schematically shown in Figure 1. First, a free-standing ultrathin SWCNT network film was obtained by pouring an SWCNT suspension onto a commercial mixed cellulose ester filter membrane and subsequently releasing it from the filter as reported in our previous publication.[33] A solution containing tetrabutyl titanate (TBT) used as the precursor of TiO_2 was then poured onto the SWCNT network film under pressure. The film was then washed with a water/ethanol mixed solution (v/v = 1:1). After being calcined at 400 °C for 4 h, the SWCNT/TiO_2 nanocomposite film was produced. The amount of TiO_2 on the SWCNT/TiO_2 film is determined by the concentration of TBT, which will affect the pore structure and surface wettability of the film. As shown in Figure 2, with an increase in the concentration of TBT, the amount of TiO_2 on the SWCNT/TiO_2 film increases. At the same time, the effective pore size of the SWCNT/TiO_2 film decreases correspondingly (Figure 2f). The amount of TiO_2 also has an effect on the water contact angle (CA) after irradiation with UV-light. With an increase in the concentration of TBT and when subjected to UV-light irradiation, the water CA decreases greatly. A 0 degree water CA is achieved when the concentration of TBT is more than 1 mM. The SWCNT/TiO_2 film prepared from 1 mM TBT is thus chosen for the study of oil-in-water emulsion separation. In this case, the pore size of the film is in the range of 20−60 nm and the thickness of the film is around 60 nm, as measured by AFM (Figure S1 of the Supporting Information).

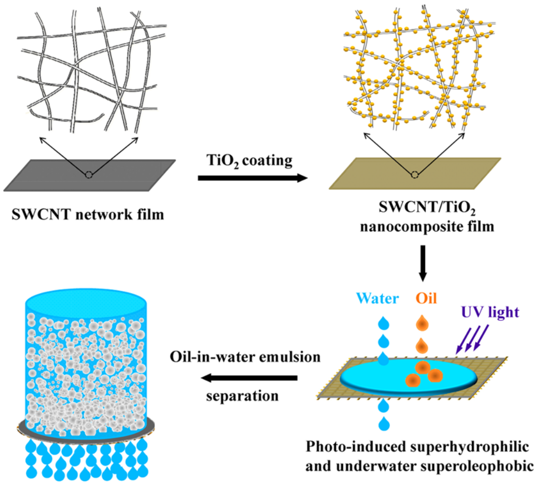

Figure 1. Schematic showing the preparation process of the SWCNT/TiO_2 nanocomposite film and for separation of an oil-in-water emulsion.

Figure 3a is a typical TEM image of the SWCNT/TiO_2 film with a thickness of 60 nm. TiO_2 nanoparticles with a diameter of several nanometers uniformly coat the surfaces of every carbon nanotube. The high-resolution TEM image of a single TiO_2 nanoparticle (inset of Figure 3a) clearly shows the fringe spacing of the TiO_2 crystal to be 0.38 nm, which corresponds to the (100) crystal plane of anatase-type TiO_2.[42,43] The effective pore size of the SWCNT/TiO_2 film ranges

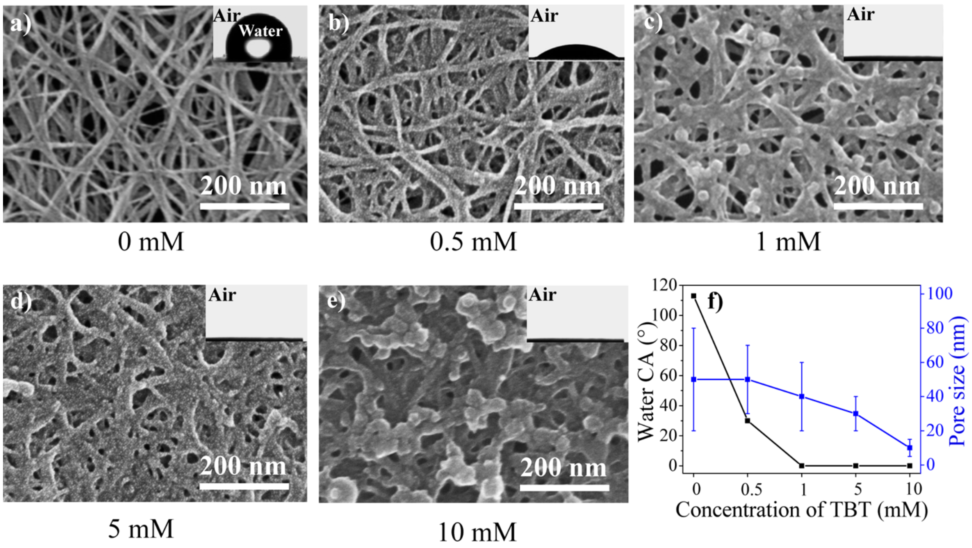

Figure 2. (a−e) SEM images of SWCNT/TiO_2 nanocomposite films corresponding to TBT concentrations of 0, 0.5, 1, 5, and 10 mM, respectively. The insets are the optical microscopy of water CA. (f) Statistical curve of effective pore size and water CA (after UV irradiation) of the film with different concentrations of TBT.

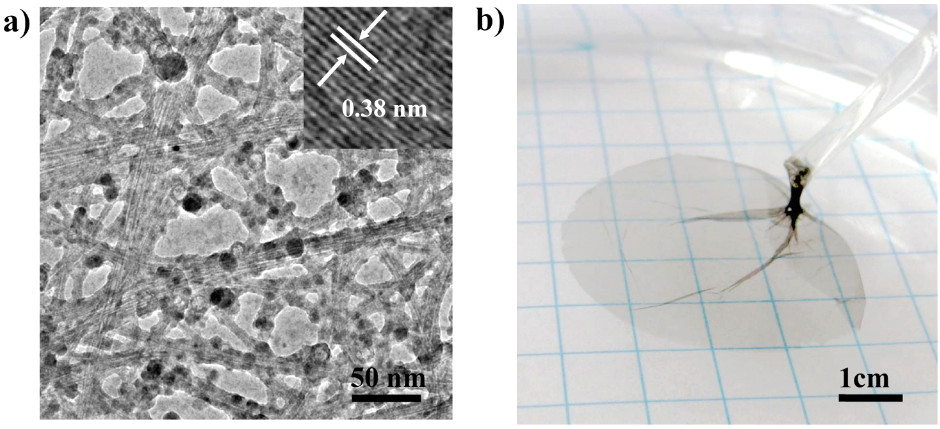

Figure 3. (a) TEM images of an SWCNT/TiO_2 nanocomposite film. The inset is the high-resolution TEM image of a TiO_2 nanoparticle. (b) Optical image of a free-standing SWCNT/TiO_2 nanocomposite film picked up by a pipet.

from 20 to 60 nm, which is smaller than that of a pristine SWCNT film due to TiO_2 coating. A free-standing SWCNT/TiO_2 film floating on the surface of an ethanol/water (1:1 v/v) mixture solution could be picked up by a pipet with no damage, indicating good flexibility of the composite film (Figure 3b).

Wettability of SWCNT/TiO_2 Nanocomposite Film. To examine the UV-induced wetting behavior of the SWCNT/TiO_2 film, the film suspended by a steel hoop was irradiated by a 300 W Hg lamp, and the water CA was measured. Figure 4a shows the variation of water CA in air with the irradiation time. The as-prepared SWCNT/TiO_2 film gives a water CA of 82° and could not be used for oil/water separation. The water CA decreases quickly upon irradiation. After 1 h, a nearly zero water CA is obtained. The superhydrophilic property of the film could last for more than 3 days in air. The UV-induced superhydrophility of the SWCNT/TiO_2 film is caused by UV-induced hydroxyl groups on the surface of the TiO_2 nanoparticles, which make the film superhydrophilic.[37,38] The UV-induced superhydrophilicity of the SWCNT/TiO_2 film is reversibly switchable (Figure 4b). When the SWCNT/TiO_2 film is placed in the dark for 7 days, its water CA recovers to 82°, and after UV irradiation, the film becomes superhydrophilic. Such a cyclic process could be repeated many times. To examine the UV-induced superwetting property, the dynamic behavior of water and oil spreading on the SWCNT/TiO_2 film was studied. As shown in Figure 5a, when a water droplet (3 μL) is placed onto the film surface in air, it spreads quickly and a near zero CA is reached. The whole process is completed within 0.32 s. When an oil droplet (1,2-dichloroethane is taken as an example) of the same volume is placed onto the film surface in air, it also spreads quickly within 0.48 s. However, the oil droplet stays on the film without spreading when placed underwater with an oil CA of 162°. These results confirm that the new SWCNT/TiO_2

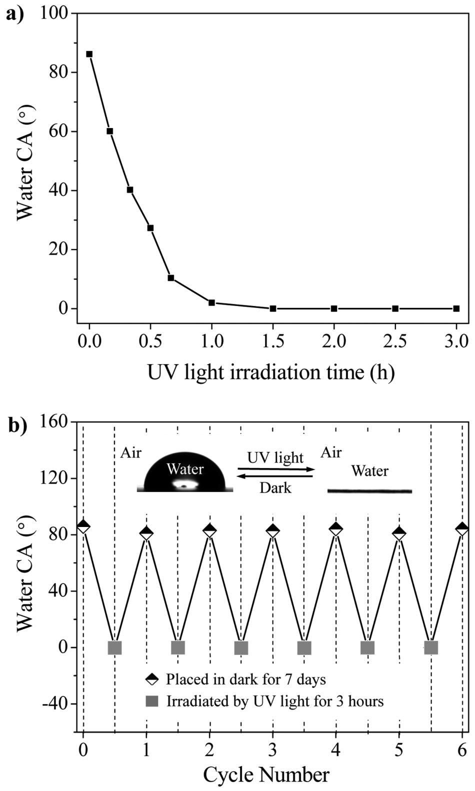

Figure 4. (a) Variation of water CA in air as a function of irradiation time. (b) Cycles of variation of water CA in the process of being irradiated by UV-light and placed in the dark.

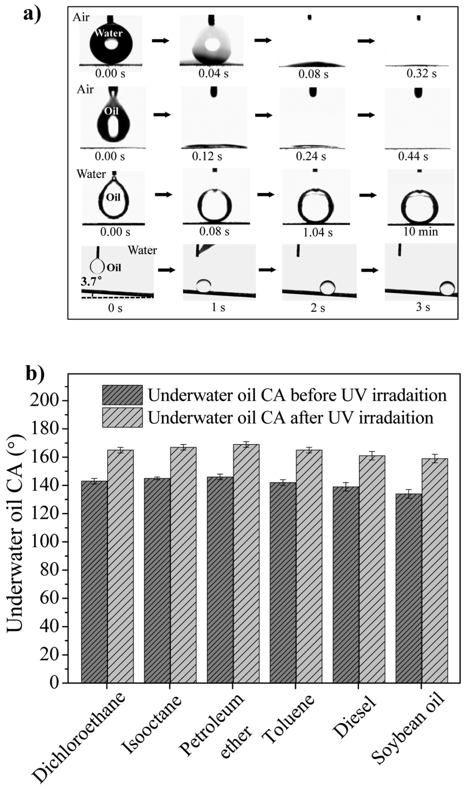

Figure 5. (a) Dynamic spreading behavior of water in air, oil in air, and underwater on an SWCNT/TiO_2 nanocomposite film after UV-irradiation. (b) Underwater oil CAs of dichloroethane, isooctane, petroleum ether, toluene, and diesel and soybean oil, respectively.

film is superhydrophilic, superoleophilic, and underwater superoleophobic after UV irradiation. The underwater CAs of six typical oils were investigated by immersing the SWCNT/TiO_2 film in water and placing an oil droplet onto it. As shown in Figure 5b, the underwater oil CAs are all >150° for different kinds of oil phases, among which petroleum ether gives an underwater CA of 169°. The underwater oil-adhesion force on the UV-irradiated SWCNT/TiO_2 nanocomposite film is extremely low (Figure S2), demonstrating that the SWCNT/TiO_2 nanocomposite film has a superior underwater anti-oil adhesion property.

Separation of Oil-in-Water Emulsion by SWCNT/TiO_2 Nanocomposite Film. The specific superwetting behavior of the SWCNT/TiO_2 nanocomposite film provides it with the ability to separate oil and water. Five surfactant-free emulsions, isooctane in water, petroleum ether in water, toluene in water, diesel in water, and soybean oil in water, and two surfactant-stabilized emulsions, sodium dodecyl sulfonate (SDS)-stabilized hexadecane in water and SDS-stabilized isooctane in water, were prepared. The as-prepared emulsions were then poured onto the SWCNT/TiO_2 nanocomposite film to carry out filtration separation under 5 kPa transmembrane pressure. The oil contents in filtrates after separation were measured *via* a total organic carbon (TOC) analyzer. It is worthy to note that the TOC value is the sum of both oil and surfactant residues in the filtrate. The residual SDS in the filtrate is determined to be around 60 ppm, obtained by a conductivity test. The oil content in the filtrate is thus obtained by subtracting the content of residual SDS from the TOC value. As shown in Figure 6a, the oil contents in the filtrates are all below 40 ppm for both the surfactant-free and the surfactant-stabilized oil-in-water emulsions. The oil contents in the filtrates are even as low as 8.9 and 4.3 ppm in surfactant-free petroleum ether-in-water and toluene-in-water emulsions, respectively. The oil contents in the filtrates for surfactant-stabilized hexadecane-in-water and isooctane-in-water emulsions are 15 and 14 ppm, respectively. Dynamic light scattering (DLS) measurement shows that the droplet size of the original surfactant-stabilized hexadecane-in-water emulsion is in the range of 100 nm to 3 μm (Figure S3a). After separation, there are almost no droplets larger than 100 nm observed in the collected filtrate (Figure S3b), further indicating the high separation efficiency. According to the discharge standards of the Environment Protection Agency of the U.S. for offshore oil and gas activities in the eastern Gulf of Mexico, a daily maximum oil limitation of produced water discharges is 42 ppm for oil and grease.[44] A similar regulation made by the Ministry of Environmental Protection of the People's Republic of China provides that the discharge standard for wastewater from offshore petroleum development industry is 45 ppm in a day.[45] Our values are all lower than the standard minimum requirements of these regulations for wastewater discharging. The fluxes of the film were calculated by measuring the time needed for complete filtration of various emulsions. As shown in Figure 6b, all the emulsions exhibit extremely high fluxes: 31 450 L m^{-2} h^{-1} bar^{-1} for a surfactant-free isooctane-in-water emulsion, 32 540 L m^{-2} h^{-1} bar^{-1} for a surfactant-free petroleum ether-in-water emulsion, 26 410 L m^{-2} h^{-1} bar^{-1} for a surfactant-free toluene-in-water emulsion, 14 880 L m^{-2} h^{-1} bar^{-1} for a surfactant-free diesel-in-water emulsion, and 10 320 L m^{-2} h^{-1} bar^{-1} for a surfactant-free soybean oil-in-water emulsion. As for the two surfactant-stabilized emulsions, the fluxes 15 690 and 17 560 L m^{-2} h^{-1} bar^{-1} are achieved for hexadecane-in-water and isooctane-in-water emulsions, respectively. These values are 2 orders of magnitude higher than commercial filtration membranes with similar rejection properties.[46−49] The flux difference between various emulsions is mainly caused by the different viscosity of oils (see Table S1). Basically, an oil-in-water emulsion with a lower oil viscosity exhibits higher flux (Figure S4). This is consistent with the Hagen−Poiseuille equation, where the flux of a liquid is inversely proportional to its viscosity.[18] To further see the oil/water separation effect, optical microscopy was used to observe the difference between the original emulsions and the collected filtrates (Figure S5). Dense oil droplets at the micrometer and submicrometer scale are observed clearly in the emulsion feeds. However, in the collected filtrates, no droplets are observed.

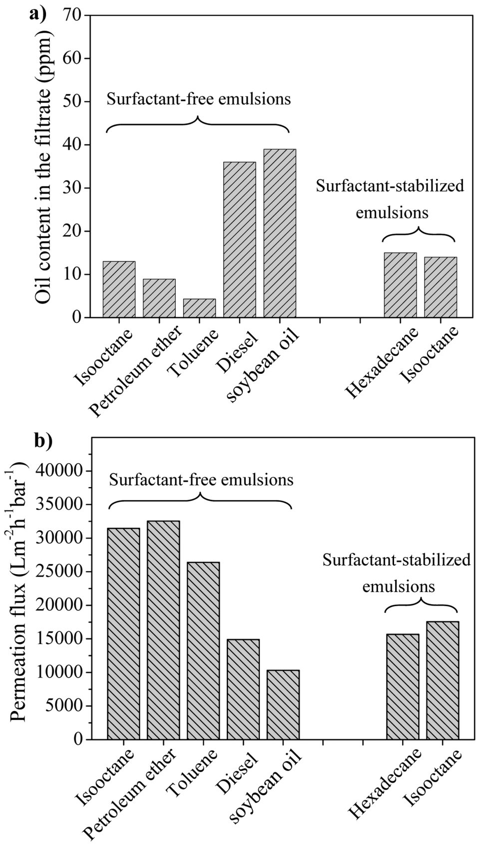

Figure 6. (a) Oil contents in the filtrates and (b) permeation fluxes of both surfactant-free and surfactant-stabilized oil-in-water emulsions separated by an SWCNT/TiO_2 nanocomposite film.

Antifouling and Self-Cleaning Performance of SWCNT/TiO_2 Nanocomposite Film. As for oil/water separation, traditional

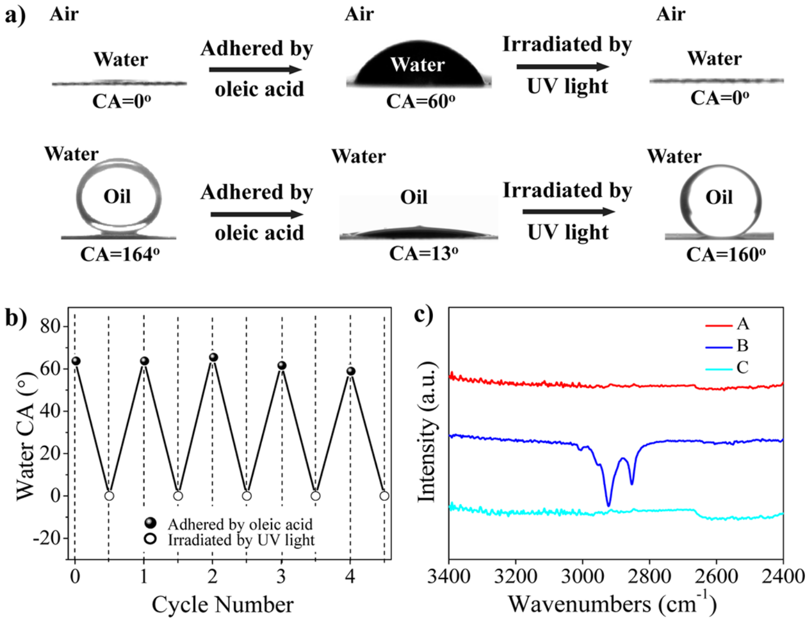

Figure 7. Antifouling property of the SWCNT/TiO_2 nanocomposite film under UV-light irradiation. (a) Water CAs and underwater oil CAs of the film after being adhered by oleic oil and subsequently irradiated by UV-light. (b) Cycles of variation of water CA in the process of being adhered by oleic oil and subsequently irradiated by UV-light. (c) ATR-FTIR spectra of the original SWCNT/TiO_2 film (A), SWCNT/TiO_2 film adhered by oleic acid (B), and subsequently irradiated by UV-light (C).

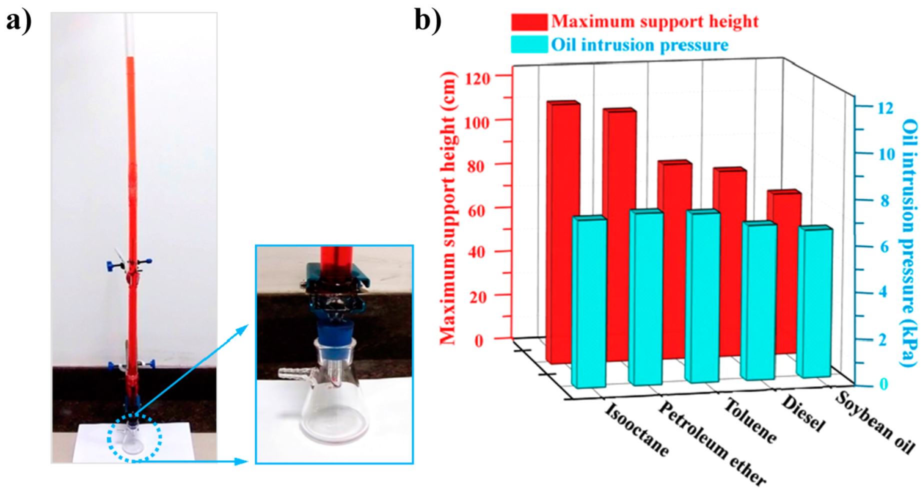

Figure 8. (a) Photograph of an SWCNT/TiO_2 nanocomposite film with an area of 2.54 cm^2 supporting an isooctane column of 115 cm in height. (b) Maximum support height and intrusion pressures of the SWCNT/TiO_2 film for various oils.

filtration membranes always suffer from fouling issues due to oil adhesion, which seriously restricts the membrane from repeated and long-term use.[14,50−52] The characteristic of TiO_2 for photocatalytic degradation of organic compounds endows the SWCNT/TiO_2 nanocomposite film with an excellent antifouling performance and self-cleaning property, which is very important for practical application. To test these properties, oleic acid, with a low volatility, was chosen as a model oil to "pollute" the film first and then subjected to UV irradiation. During this process, the variation of water CAs in air and underwater oil CAs of the film was monitored (Figure 7a). The original SWCNT/TiO_2 nanocomposite film shows a nearly zero water CA in air and an underwater oil CA of 164° after UV-light irradiation. After being adhered by oleic acid, its water CA increases to 60° and its underwater oil CA decreases to 13°, indicating the adhesion of oleic acid on the film. When the contaminated film is irradiated by UV-light for 5 h, the film recovers to be superhydrophilic and underwater superoleophobic again. This process has been repeated several times without change of wettability, as can be seen in Figure 7b. To further confirm the process of photocatalytic degradation of oleic acid by the SWCNT/TiO_2 nanocomposite film, ATR-FTIR spectra were measured. As shown in Figure 7c, the original SWCNT/TiO_2 nanocomposite film has no obvious peaks in the range 2800−3000 cm^{-1}. After the film is adhered by oleic acid, two characteristic peaks at 2853 and 2922 cm^{-1} ascribed to the stretching vibration of $-CH_3$ and $-CH_2-$ of the oleic acid molecule are clearly observed in the case of oleic acid-polluted film.[53] The characteristic peaks completely disappear after UV-light irradiation for 5 h, indicating the photodegradation of oleic acid. However, theh pure SWCNT film does not show the photocatalytic and antifouling properties (Figure S6). The photodegradation of other surfactants (Tween 80 is taken as an example here) further demonstrates the antifouling performance and self-cleaning property of the SWCNT/TiO_2 nanocomposite film (Figure S7).

Oil Intrusion Pressure of SWCNT/TiO_2 Nanocomposite Film. The intrusion pressure, which indicates the maximum height of liquid that the membrane can support, is another important parameter for practical operation. The intrusion pressures of our SWCNT/TiO_2 nanocomposite film for various oils were measured by pouring oil onto a water-immersed SWCNT/TiO_2 film to the maximum height (Figure 8a). The intrusion pressure (P_{int}) was calculated by using the equation

$$P_{int} = \rho g h_{max} \tag{2}$$

where ρ is the density of the oil, g is the acceleration of gravity, and h_{max} is the maximum height of oil the membrane can support.[41,54] The results are shown in Figure 8b. The oils show intrusion pressures of around 6−7 kPa, which corresponds to at least 72 cm maximum liquid height in the case of soybean oil and 115 cm maximum liquid height in the case of isooctane. This indicates there is enough operation potential for separation of oil-in-water emulsions *via* the SWCNT/TiO_2 nanocomposite film as long as the applied transmembrane pressure is lower than the oil intrusion pressure.

CONCLUSIONS

We have successfully developed an ultrathin and flexible film based on an SWCNT/TiO_2 nanocomposite network. With the aid of UV-light irradiation, the ultrathin network film is superhydrophilic and underwater superolephobic and can effectively separate both surfactant-free and surfactant-stabilized oil-in-water emulsions with a wide range of droplet sizes. With adequate film thickness and nanoscale pore size of the SWCNT/TiO_2 composite network film, a vey high flux rate, up to 30 000 L m^{-2} h^{-1} bar^{-1}, and an ultrahigh separation efficiency 99.99% were achieved.

The characteristic of TiO_2 for photocatalytic degradation of organic compounds endows the SWCNT/TiO_2 film with an excellent antifouling and self-cleaning property even after being contaminated with oils, indicating the potential of our SWCNT/TiO_2 for removing oil from oil/water emulsions at industrial scales. Oil/water separation, especially separating oil from emulsified oil/water mixtures, is extremely important and highly demanded by many industries. As an alternative to conventional polymer-dominated filtration membranes, our work points in a direction for making ultrathin and superwetting membranes to remove oil from oil/water emulsions.

METHODS

Materials. The SWCNT (o.d. <2 nm, length: 5−30 μm, purity: >95%) used in this work was a commercial product supplied by XF Nano, Inc, China. Diesel and soybean oil were commercial products. All other chemicals were of analytical grade, commercially available from Shanghai Chemical Reagent Co. Ltd., and used as received without further purification.

Fabrication of SWCNT/TiO_2 Nanocomposite Network Film. The SWCNT dispersion was first prepared by mixing 0.1 mg/mL SWCNT powder, 1 mg/mL sodium dodecyl benzenesulfonate, and deionized water and sonicating the mixture for 10 h under a power of 2 kW. To obtain the SWCNT dispersion with a better dispersion degree, the as-prepared SWCNT dispersion was centrifuged for 30 min at 10 000 rpm. The supernatant solution was collected for the following experiments. The SWCNT film was prepared *via* a wet process where 50 mL of diluted SWCNT dispersion with a concentration of 0.6 mg/L was filtered onto a commercial mixed cellulose ester filter membrane with a pore size of 0.45 μm and diameter of 3.8 cm. The SWCNT film was then released from the MCE filter membrane, transferred onto a copper mesh (pore size: ∼25 μm), and fixed on a vacuum filter apparatus. Tetrabutyl titanate in ethanol with different concentrations was poured onto the SWCNT film under the applied transmembrane pressure of 10 kPa. The obtained film was washed with a water/ethanol mixed solution (v/v = 1:1). Finally, the film was calcined at 400 °C for 4 h in order to obtain TiO_2 nanocrystals, and the SWCNT/TiO_2 nanocomposite film was produced.

Preparation of Oil-in-Water Emulsions. The surfactant-free oil-in-water emulsions were prepared by mixing water and oil in a volume ratio of 9:1 and sonicating the mixtures for 0.5 h under a power of 2 kW to produce a white, milky solution. Isooctane, petroleum ether, toluene, and diesel and soybean oil were used as the typical oil phase, respectively. All emulsions were stable for more than 12 h and were used for separation directly. The surfactant-stabilized oil-in-water emulsions were prepared by mixing either hexadecane or isooctane with water in a volume ratio of 1:99. Sodium dodecyl sulfonate with a concentration of 0.1 mg/mL was added into the mixture as an emulsifier. The solution was stirred at a speed of 2000 rpm for 5 h to produce a milky emulsion. Both of the emulsions were stable for more than 1 month.

Oil-in-Water Emulsion Separation. The separation process was carried out on a vacuum filter apparatus equipped with an SWCNT/TiO_2 nanocomposite film (separation area is 2.54 cm^2). Before the separation process, the SWCNT/TiO_2 nanocomposite film was irradiated by UV-light (a 300 W Hg lamp as the light source) for 3 h, where the lamp was placed on the top of the film at a distance of 25 cm. The surface wettability of the film was measured during this process. A 25 mL amount of an oil-in-water emulsion was poured into the filter, and the separation was achieved driven by a pressure difference of 5 kPa. The filtrate water was collected, and the oil content in the water was determined.

Characterization. SEM was measured on a field-emission scanning electron microscope (Hitachi S4800, Japan). TEM was conducted on a Tecnai G2 F20 S-Twin field-emission transmission electron microscope. Optical microscopy images were taken with a Nikon AZ100. Contact angles were measured on an OCA20 machine (Data-physics, Germany). For the underwater oil CA measurement, the film was first immersed in water. Oil droplets (3 μL) of isooctane, petroleum ether, toluene, diesel oil, and soybean oil were then dropped carefully onto the film from the bottom, respectively, and then the CAs were measured. For each value, three measurements per sample were done, and the average value was obtained. The oil content in the filtrate was detected on a total organic carbon analyzer (Aurora 1030W, USA). The dynamic light scattering was measured on a Malvern Zen 3600.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Thickness of the SWCNT/TiO_2 nanocomposite film; underwater oil-adhesion force on the photoirradiated SWCNT/TiO_2 nanocomposite film; droplet size distribution of surfactant-stabilized emulsions in the feed and filtrate; summary of the composition and oil droplet size of the emulsions; relationship between permeation flux of the oil-in-water emulsion and oil viscosity; optical images of the emulsions before and after separation; whether the pure SWCNT film has photocatalytic and antifouling properties; photodegradation of common surfactants by the SWCNT/TiO_2 nanocomposite film; surfactant adsorption on a film surface after filtration. These materials are available free of charge *via* the Internet at http://pubs.acs.org.

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