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CNTs/TiO_2 composite membrane with adaptable wettability for on-demand oil/water separation

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ABSTRACT

Pre-wetting induced separation membranes are of great significance due to their unique property for separating oil/water mixtures. Herein, we have presented a facile strategy to prepare a separation membrane by integrating carbon nanotubes (CNTs) and titanium dioxide nanoparticles (TiO_2 NPs). The obtained CNTs/TiO_2 composite membrane has presented smart wettability to activate on-demand separation for expected components from oil/water mixtures. In addition, it can maintain its separation efficiency above 99.1% even after ten cyclic separations. It is rather remarkable that this composite membrane has taken on excellent separation performance with the flux up to 40,000 L m^{-2} h^{-1} $bar^{-1}$for water-in-dichloromethane emulsion and separation efficiency above 98.89%, which has surpassed most of the reported separation membranes to date. Furthermore, the CNTs/TiO_2 membrane has feathered excellent corrosion resistance ability under harsh conditions (HCl, NaOH, NaCl) for 7 days, and can show stable permeation flux and efficiency towards various emulsions. This work will provide further guidance for developing CNTs-based membranes in order to realize task-oriented oily water treatment.

1. Introduction

The ever-growing industrial organic pollutants have brought serious water pollution, which has caused severe harm to the ecological environment (Li et al., 2018). Special membranes with opposite wettability toward oil and water have been regarded as promising materials for gaining the desired ingredient from the oil/water mixtures (Liu et al., 2017; Jing and Guo, 2018). Superhydrophobic/superoleophilic membranes can obtain oil from water-in-oil (W/O) emulsions (Yu et al., 2017; Cai et al., 2020; Cao et al., 2019; Zhang et al., 2020). But they are inapplicable for separating water-in-oil emulsions with light density because the demulsified water usually forms a blocking layer across the membrane (Li et al., 2016; Wang et al., 2020). In addition, their micro/nano channels are easily blocked because of their lipophilic essences (Chen et al., 2019; Lin and Hong, 2019). Superhydrophilic/underwater superoleophobic membranes have provided an efficacious pathway to solve these problems (Li et al., 2020a; Liao et al., 2017; Liu et al., 2018). Nevertheless, they are difficult to obtain water from heavy oil-in-water (O/W) emulsions. This is owing to the demulsified oil will form a layer to hinder the water phase passing through the membrane. Therefore, developing advanced

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separation membranes with adjustable wettability is vital for oil/water separation (Bao et al., 2020; Zhu et al., 2018).

The chemical component and interface roughness are regarded as two critical factors to allow the materials with distinctive affinities towards oils and water (Ghasemlou et al., 2019; Wei et al., 2018). In recent years, materials with special structure and chemical property for selective oil/water separation have experienced rapid development. Janus membranes with asymmetric structure on each side can realize switchable oil/water separation by adjusting their corresponding wetting surfaces towards oil/water mixtures (Yang et al., 2019a,b; Zhang et al., 2019). For example, Feng et al. have fabricated a Janus membrane through depositing the photoactive layer on the various surfaces. Therefore, it can tailor the wettability in the presence of UV irradiation and realize the on-demand emulsion separation (Zhang et al., 2019). However, they are suffered from issues for the practical manipulation to achieve switchable separation. Apart from the Janus membranes, stimuli-responsive materials can perfect control their surface wettability via changing the external environment (Pan et al., 2019; Wang et al., 2018). For instance, a multi-responsive magnetic material was prepared (Lü et al., 2020), to realize the controllable separation of various oil/water mixtures by adjusting the pH environment. Moreover, the magnetic Fe_3O_4 can also increase the separation efficiency (Kozlovskiy et al., 2019). Nonetheless, their separation efficiency is highly governed by the properties of the oil/water mixtures, such as density and viscosity. Besides, their special device equipment and massive energy consumption (light, electric field or heating) have further limited their development.

Fortunately, superamphiphilic membranes have offered feasible solutions to the aforementioned dilemma. Their wettability can be adjusted from superamphiphilicity in the air to superamphiphobicity under water or under oil after being pre-wetted with water or oil. Hence, they can selectively gain the required component only by changing the relative density of water and oil. For example, a superamphiphilic titanium dioxide/cobaltosic oxide/graphene oxide (TiO_2/Co_3O_4/GO) composite membrane has been developed via solvent thermal synthesis (Bao et al., 2020). This membrane can separate different types of oil-in-water emulsions. Furthermore, it can realize the photodegradation of dyes molecular with the efficiency about 96.5% attributing to the large specific surface area and plentiful active sites. A polydopamine functionalized steel mesh superamphiphilic membrane was prepared by using the dip-coating method (Li et al., 2020b). The membrane has the capacity to separate various emulsified oil/water systems. Xu et al. have fabricated a Bi/PDA@PT electrospun membrane (Ying et al., 2020), which can separate each type of emulsions selectively and efficiently. In spite of this, the complex preparation process and single separation mode have limited their further advance. Moreover, they are faced with the weakness of antifouling property in an acidic or alkaline environment. Therefore, to develop a separation membrane through an easy method for controllable oil/water purification with comprehensive performances, including efficiency, permeability, recyclability, and antifouling capability, is of great urgency.

Carbon nanotubes (CNTs), have gained increasing attentions due to their prominent properties. Herein, we have reported a superamphiphilic membrane by integrating CNTs and titanium dioxide nanoparticles (TiO_2 NPs) through in-situ growth TiO_2 NPs on the CNTs surface (Fig. 1A) and afterward vacuum-assisted filtration. The CNTs/TiO_2 composite membrane has presented underwater superoleophobicity and underoil superhydrophobicity via combination of CNTs with micro/nano structure and TiO_2 NPs with high surface energy (Lai et al., 2016). Therefore, it can realize multitasking separation performance for immiscible or emulsified oil/water mixtures (Fig. 1C). Furthermore, the CNTs/TiO_2 composite membrane has shown superior separation ability for W/O emulsions with flux reaching up to 40,000 L m^{-2} h^{-1} bar^{-1}. In addition, it presented antifouling ability after being immersed in harsh environments for several days.

2. Experimental details

2.1. Materials

Carbon nanotubes (CNTs, 10–30 nm diameter, containing -carboxyl with 2.0 wt%) were provided from Chengdu Organic Chemistry Co. Ltd. Titanium oxysulfate ($TiOSO_4$) was attained from Alfa Aesar (China) Co. Ltd. Other chemical reagents were got form Sinopharm Chemical Reagent Co. Ltd. PVDF (0.45 μm aperture, 125 μm thicknesses) substance was provided by Millipore Industrial & Lab Chemicals.

2.2. Construction of the CNTs/TiO_2 composite membrane (Fig. S1)

The CNTs/TiO_2 membrane was prepared through one-pot method and subsequent suction filtration. Briefly, CNTs (80 mg) were dispersed into water (200 mL) and stirred for 100 min under 25 °C to form a uniform CNTs dispersion. Then, different amounts of $TiOSO_4$ (320 mg, 640 mg, 960 mg, 1280 mg, 1600 mg) were added and stirring for 2 h. At this process, $TiOSO_4$ solution were completed changed into $TiO(OH)_2$ via hydrolysis in water. Finally, CNTs/TiO_2 composites were obtained after thermal treatment to 300 °C for 2 h. The resultant composites were filtrated on a PVDF substance and dried under 40 °C for 0.5 h.

2.3. Separation experiment for immiscible oil/water mixtures (Table S1)

The organic solvents (including toluene, hexane, chloroform and tetrachloromethane) were dyed with Oil red O. The water was colored by $CuSO_4$. They were mixed (1:1, v/v) to form toluene/water mixture (T/W), hexane/water mixture (H/W), chloroform/water mixture (C/W), tetrachloromethane/water mixture (TC/W), respectively. They were poured onto the separation system pretreated with water or oil, respectively.

2.4. Separation experiment for W/O emulsions and O/W emulsions (Table S2)

With regard to W/O emulsions, 1.0 g of span 80, 120 mL of oil (including dichloromethane, chloroform, carbon tetrachloride and 1,2-dichloroethane) and 1 mL of water were mixed together to form water-in-dichloromethane (W/D) emulsion, water-in-chloroform (W/C) emulsion, water-in-tetrachloromethane (W/Ct) emulsion and water-in-1, 2-dichloroethane (W/Dc) emulsion, respectively. Similarly, for O/W emulsions, 1.0 g tween 80, 120 mL of water and 1 mL of oil (heptane, petroleum ether, dichloromethane and chloroform) were successively mixed to prepare heptane-in-water (Hp/W) emulsion, petroleum ether-in-water (Pe/W) emulsion, dichloromethane-in-water (D/W) emulsion and chloroform-in-water (C/W) emulsion, respectively. Each emulsion was vigorous stirred for 8 h to form a uniform system. The separation experiments were taken on a vacuum filter apparatus under 0.02 MPa for W/O emulsions and under gravity for O/W emulsions.

2.5. Characterizations

The morphology of the CNTs before and after modification were viewed from field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and as well transmission electron microscope

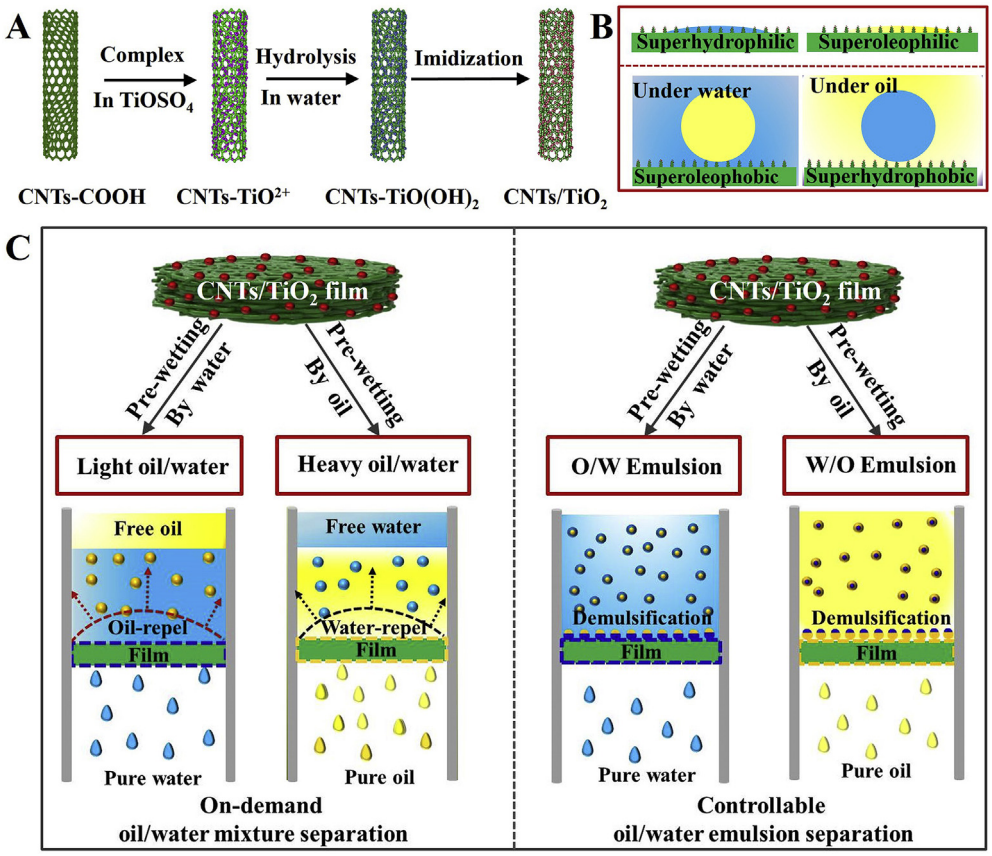

Fig. 1. (A) Schematic illustration of the construction of the CNTs/TiO_2 through a hydration-dehydration method. (B) The wettability of CNTs/TiO_2 composite membrane in the air, underwater and underoil. (C) Mechanism description of the CNTs/TiO_2 composite membrane for selectively separating oil/water mixture (left) and emulsion (right).

(TEM, JEOL2100 HR). The wettability property was got from a contact angle measurement system (OCA20, Data-physics). The chemical ingredient was analyzed and calculated using X-ray photoelectron spectroscopy (XPS, Shimadzu Axis Untraded spectroscope). X-ray diffraction was performed on an X-ray diffract meter (XRD, D8 Discover) with Cu KR radiation ($\lambda = 1.5406$ Å). The specific surface area of the CNT/TiO_2 composite was performed on the micrometric surface area analyzer (ASAP, 2020M) for N_2 gas adsorption. The size distribution of the feed and filtration was recorded by Dynamic light scattering (DLS) measurement (Nano ZS, Malvern). Optical image of the emulsions before and after separation was obtained on a microscope (BX51TF Instec H601) by dropping the solution on a wafer. The content of oil in water was monitor by UV/Vis absorption spectrophotometer (UV/Vis/NIR spectrometer, Lambda 950). Karl Fischer titrator was used to determine the content of water in feed and filtration (915 KF Ti-Touch). The oil purification in O/W emulsion was measured by a total organic carbon analyzer (TOC, LB-T200). Noting: in order to ensure the accuracy and scientificity of the results, all tests were the average of three samples.

3. Results and discussion

There were two paramount factors to dominate the wettability for realizing smart oil/water separation, structure and composition (Zarghami et al., 2019). The effect of the amount of the $TiOSO_4$ on the specific surface area of the CNTs/TiO_2 composite membranes was explored. It reached the maximum with the appropriate addition of $TiOSO_4$ (Fig. 2A). The higher surface area with suitable addition of $TiOSO_4$ will favor the good adsorption capacity of the CNTs/TiO_2 composite membrane (Kango et al., 2013; Li et al., 2013). It is particularly notorious that the electronic properties of a material are critically dependent on the average particle size of the constituents. We have further studied the influence of the amount of the $TiOSO_4$ on the micromorphology of the CNTs/TiO_2 composite membrane. The loading of the TiO_2 nanoparticles has become more obvious along with the increasing amount of the $TiOSO_4$ (Fig. S2). However, excessive amount of $TiOSO_4$ could bring about agglomerate phenomenon of the TiO_2 nanoparticles and even some can fall off from the CNTs membrane. The chemical composition of the CNTs/TiO_2 composite membrane was further monitored by XPS. Only peaks of C and O elements appeared in the CNTs membrane (Fig. S3). However, a typical Ti 2p peak was appeared at around 457 eV (Fig. 2B) in the XPS pattern of CNTs/TiO_2 composite membrane, mainly assigning to the TiO_2 (Gu et al., 2017). XRD exhibited the characteristic diffraction peaks of CNTs membrane at around 25.95° (Fig. 2C). After TiO_2 NPs modified, it was appeared at around 25.47°, which was assigned to the collective effect of CNTs and TiO_2 NPs with (101) reflection (Liu et al., 2019). The micromorphology of the CNTs/TiO_2 composite membrane was further investigated by using SEM and TEM. The pristine CNTs with an average diameter of 24 ± 5 nm were twined with each other and formed a continuous, evenly two-dimensional porous network (Fig. 2D and G). Upon being in-situ growth with TiO_2 NPs, the surface roughness increased and the diameter increased to 40 ± 3 nm (Fig. 2E and H), indicating a number of TiO_2 NPs were randomly distributed on the surface of CNTs. These nanoparticles were overlapped densely and some even deeply embed into the CNTs network (Fig. 2F). The cross-section SEM image suggested that it has formed a tight structure with 850 ± 20 nm (Fig. 2I, Fig. S4). This thin CNTs/TiO_2

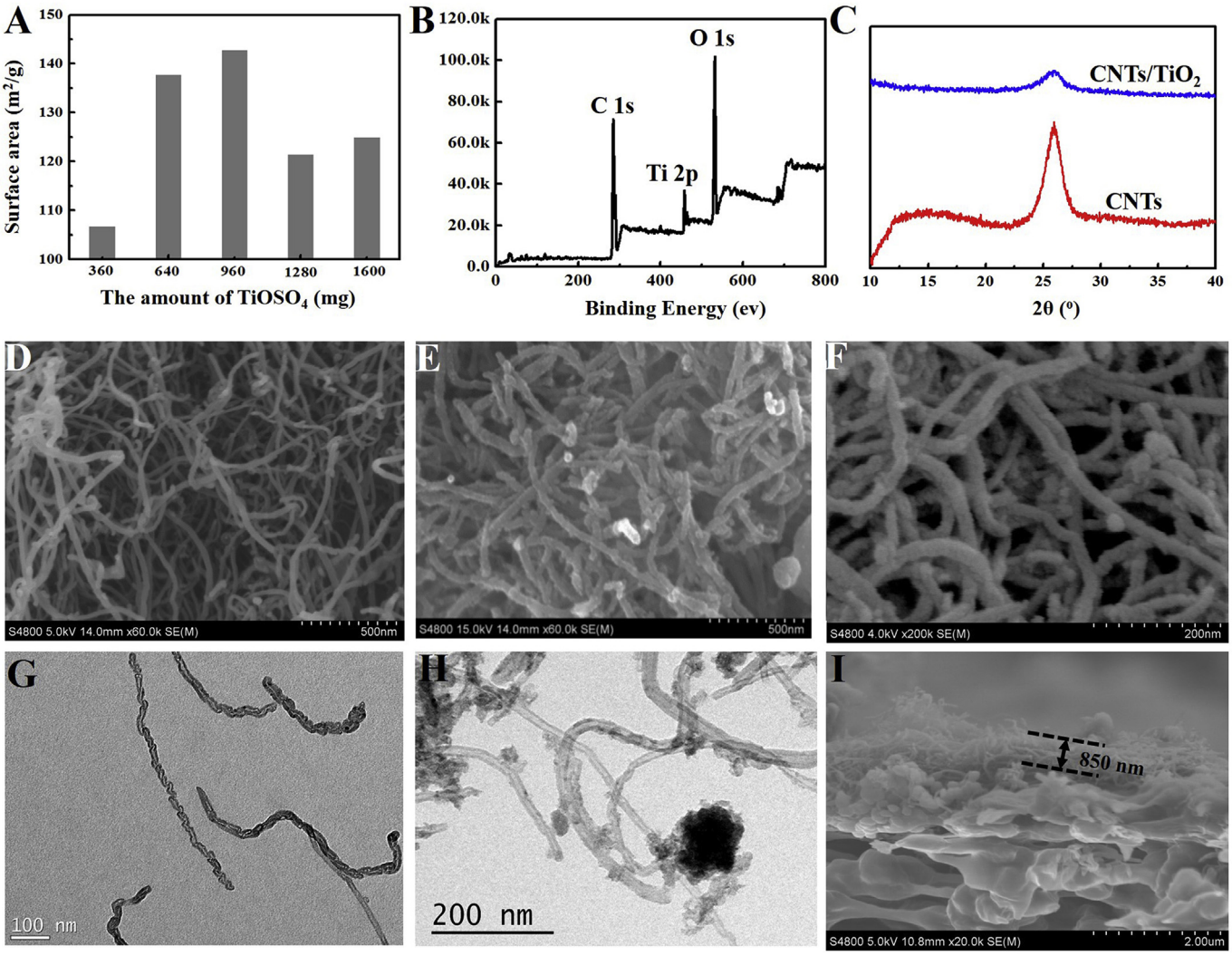

Fig. 2. (A) The surface areas of the CNTs/TiO_2 composite membrane with different amounts of $TiOSO_4$. (B) The XPS spectrum of the CNTs/TiO_2 composite membrane. (C) The XRD results of the CNTs and CNTs/TiO_2 composite membranes, respectively. The SEM images of (D) CNTs and (E) CNTs/TiO_2 membrane. (F) The amplified SEM images of the CNTs/TiO_2 composite membrane. The TEM images of (G) CNTs membrane and (H) CNTs/TiO_2 composite membrane, respectively. (I) The cross-section SEM image of the CNTs/TiO_2 composite membrane. (Note: the amount of $TiOSO_4$ was 960 mg from Fig. 2B–Fig. I).

composite membrane will offer an encouraging opportunity for oily wastewater purification.

The wettability of this composite membrane was also comprehensively assessed. It is well known that the stoichiometry of a compound determines its properties (Zdorovets et al., 2020). We investigated the influence of the amount of the $TiOSO_4$ on the wettability of the CNTs/TiO_2 composite membrane. This composite membrane was superoleophobic underwater and superhydrophobic underoil when the dosage of the $TiOSO_4$ was 960 mg (Fig. S5). The CNTs/TiO_2 composite membrane showed superamphiphilic property in the air (Fig. 3A). Both the water (Movie S1) and chloroform (Movie S2) droplets were spread out upon contacting with the membrane surface, which resulted in a contact angle of about 0°, respectively (Fig. 3B). In contrast, the CNTs/TiO_2 composite membrane has shown underwater superoleophobicity (Fig. 3C and D) and underoil superhydrophobicity (Fig. 3C and E) for all the given oils.

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To better understand its liquid-repellency property in the underwater or underoil environment, we further studied its dynamic wetting behaviors. Both the oil droplet and water droplet presented a spherical shape with contact angle 153 ± 0.8° and 154 ± 1.1°, respectively, to minimal adhesion force when they were preloaded onto the membrane surface (Fig. 4A and B). It was difficult to make the water (chloroform) attach on the surface of this composite membrane under hexane (water) (Movie S3 and Movie S4). This particular wettability is mainly owing to the chemical constituents and rough architecture of this membrane. On the one hand, TiO_2 NPs were lyophilic towards water and oil (Ma et al., 2016). On the other hand, the rough construction deriving from the TiO_2 NPs can enhance the wettability of CNTs membrane. Therefore, the CNTs/TiO_2 composite membrane was infiltrated with water, resulting in blocking effective contact between oil and membrane surface (Fig. 4C) (Kango et al., 2013). Similarly, the trapped oil phase was served as a repulsive layer to effectively restrain water penetration (Fig. 4D) (Cai et al., 2017).

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The controllable wettability has endowed the CNTs/TiO_2 composite membrane a foreground material for switchable oil/water separation only by pre-wetting. The hexane phase has shown a

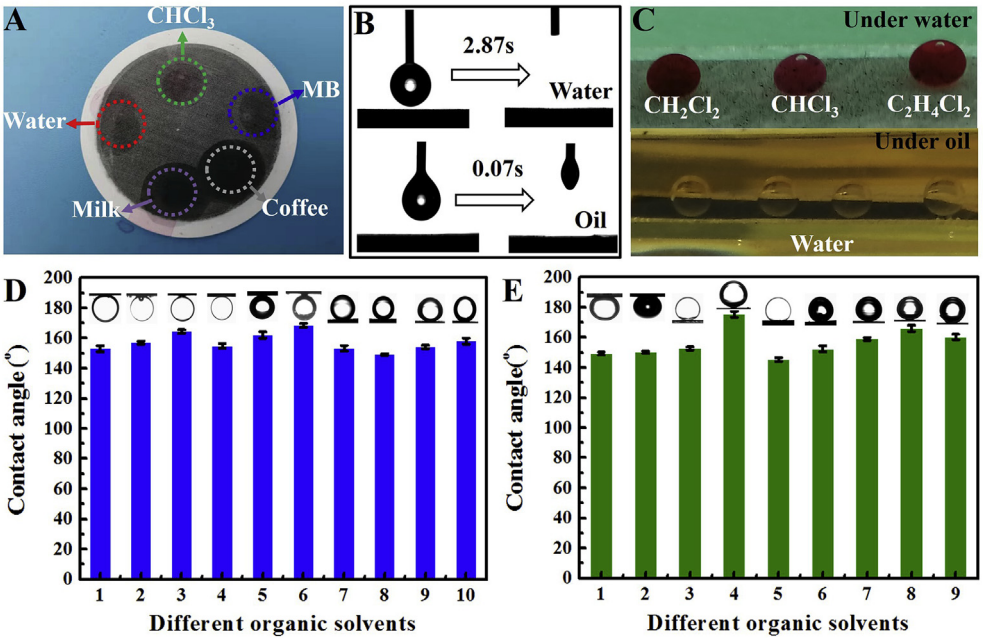

Fig. 3. (A) A Photograph of different liquids on the CNTs/TiO_2 composite membrane in the air. (B) The wettability of the water and chloroform on the CNTs/TiO_2 composite membrane, respectively. (C) Photographs of different liquids on the CNTs/TiO_2 composite membrane under water (up) and oil (down), respectively. (D) The contact angle of various organic solvents on the surface of CNTs/TiO_2 composite membranes underwater (1-petroleum ether, 2-heptane, 3-silicone oil, 4-hexane, 5-toluene, 6-edible oil, 7-dichloromethane, 8-chloroform, 9-tetrachloromethane, 10–1, 2-dichloroethane). (E) The wettability of water s on the CNTs/TiO_2 composite membrane under different oils (1-dichloromethane, 2-chloroform, 3-heptane, 4-silicone oil, 5-hexane, 6-toluene, 7- paraffin oil, 8-edible oil, 9-pump oil).

highly spherical shape on the water-trapped membrane, whereas the water phase permeated through the CNTs/TiO_2 composite membrane under only gravity-driven (Fig. 5A). Analogously, as to heavy oil/water mixture, the water droplets were rejected on the oil-trapped membrane surface, and the chloroform droplets passed through this composite membrane (Fig. 5B). The CNTs/TiO_2 composite membrane also has presented excellent separation capacity for other oil/water mixtures (Fig. 5C). The reliability of the CNTs/TiO_2 composite membrane was further tested, which was an important criterion for practical application. The CNTs/TiO_2 composite membrane maintained its good separation efficiency after ten cycle's separation (Fig. 5D). In addition, there was almost no change about the surface macrostructure and wettability of this composite membrane after ten cyclic separations (Fig. S6). Hence, it can be deduced that the TiO_2 NPs were stably modified on the CNTs network, and the separation cannot destroy its chemical composition and the rough structure.

The oil/water mixtures separation mechanism of CNTs/TiO_2

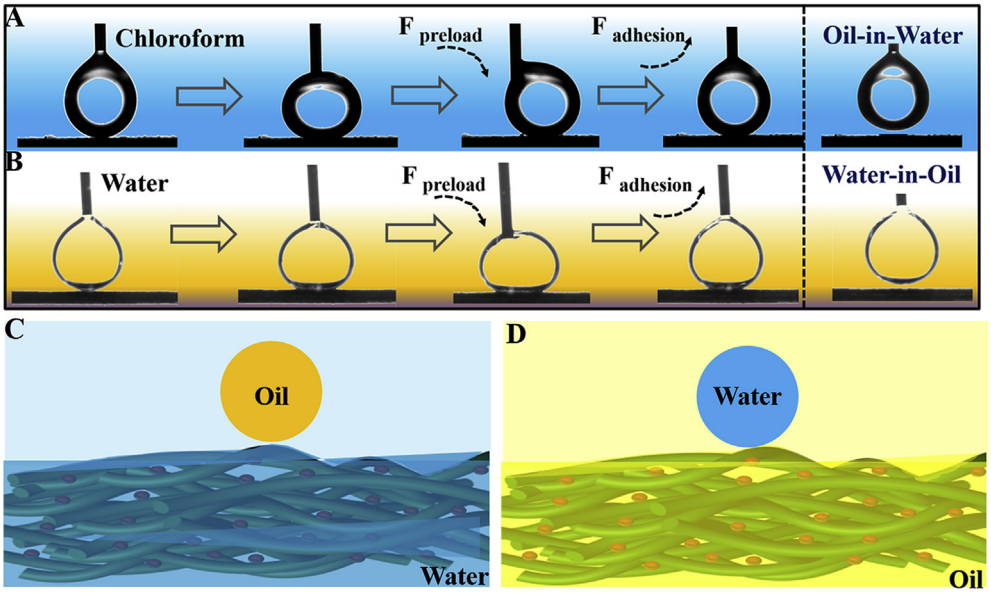

Fig. 4. Underwater chloroform (A) and underoil (heptane) water (B) dynamic adhesion process on the CNTs/TiO_2 composite membrane. (C–D) Schematic diagrams of special wettability of the CNTs/TiO_2 composite membrane.

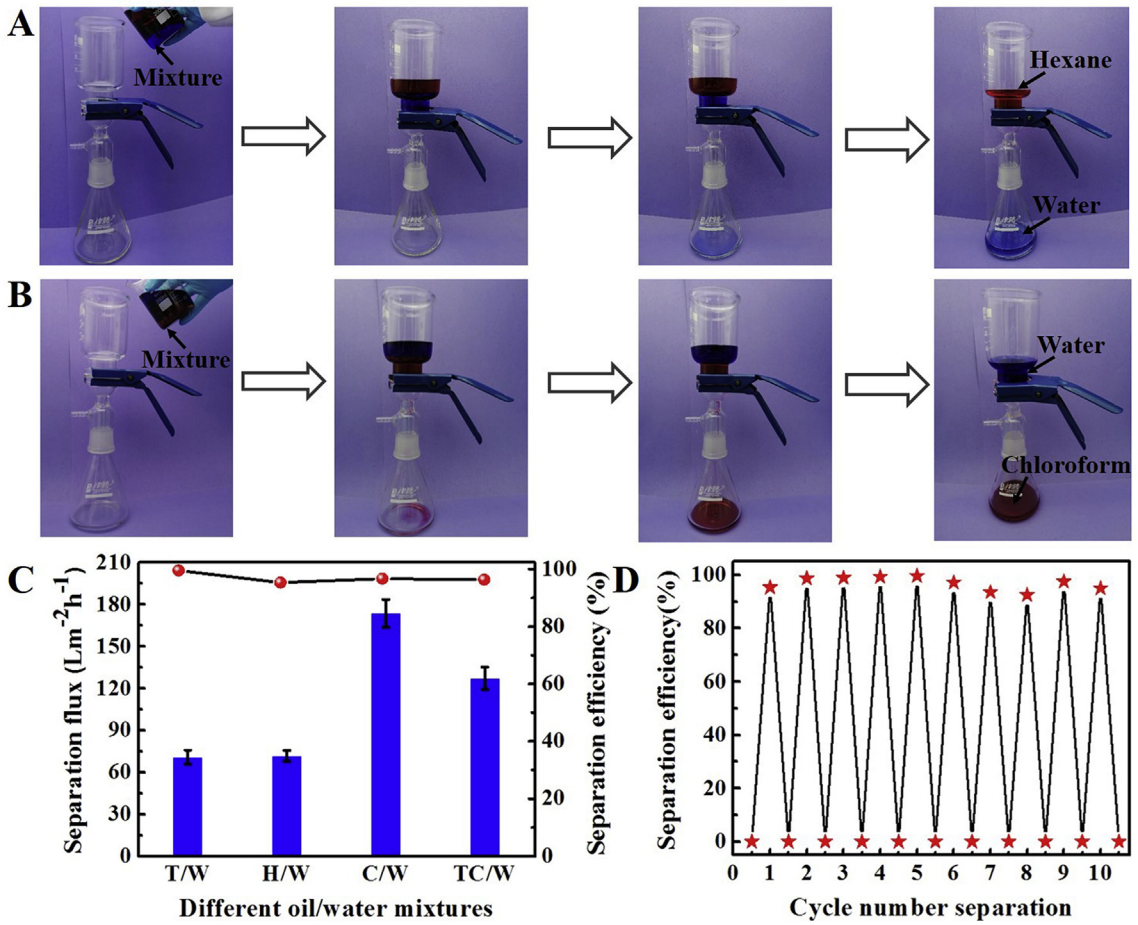

Fig. 5. (A) Photographs of the separation of n-hexane/water mixture using the CNTs/TiO_2 composite membrane. The water quickly passed but the oil was prevented. (B) Photographs of chloroform/water mixture separation using the CNTs/TiO_2 composite membrane. The oil rapidly passed through, whereas the water was collected. (C) The separation flux and efficiency of a variety of mixtures. (D) The cyclic separation efficiency of hexane/water mixture.

composite membrane is deduced as follows. The water or oil phase will permeate the membrane spontaneously under the capillary effect ($\Delta P < 0$) of porous structure (Fig. 6A and B). Hence, the CNTs/TiO_2 composite membrane was superamphiphilic in the air. However, this membrane was captured by the oil or water after being pre-wetted with the corresponding liquid. Under this case, this membrane has presented liquid-repellent property with θ larger than 90° and can sustain some pressure ($\Delta P > 0$) (Fig. 6C and D). Therefore, the pre-wetted CNTs/TiO_2 composite membrane can prevent the second liquid with the opposite polarity entering through the membrane (Li et al., 2016).

The emulsified droplets are more easily to form and be trapped into a micro/nano network structure. Therefore, it remains a rigorous challenge to realize the effective separation of different types of emulsions. The emulsion separation performance of this membrane with tailored wettability was investigated. In this work, water-in-chloroform (W/C) emulsion was acted as a model W/O emulsion to assess its separation effectiveness. The feed emulsion has shown milky white, whereas the collected filtrate was almost transparent (Fig. S7). The separation ability was qualitatively analyzed by using the optical microscopy and DLS. There were densely packed droplets in the feed solution (Fig. 7A, Figs. S8–S9), whereas no droplets were observed after separation, indicating its excellent separating efficiency. The emulsion droplets de-emulsified once touching the membrane surface, and the oil phase rapidly passed through the membrane, and the water phase was rejected above the membrane (Fig. 7G). The purity and the flux were also calculated to evaluate its separation performance quantitatively. As displayed in Fig. 7B and C, the purity of the oil kept above 98.89%, as well as the flux maintained 28,000 L m^{-2} h^{-1} bar^{-1}, even cyclic separation. Similar separations were also achieved for other emulsions (Figs. S8–S9), such as water-in-dichloromethane (W/D) emulsion, water-in-tetrachloromethane (W/Ct) emulsion and water-in-1, 2-dichloroethane (W/Dc) emulsion. The separation flux of W/D emulsion was higher than other types of W/O emulsions because the permeate ability for W/O emulsions is primarily dominated by the viscosity of oil (Table S3). It was noted that its separation throughput for W/O emulsions can attain to 40,000 L m^{-2} h^{-1} bar^{-1}, which went beyond the reported membranes reported as yet (Tables S5–S6).

Furthermore, we have investigated the effect of the loading methods of TiO_2 nanoparticles on the separation performance of water-in-oil emulsion. The CNTs/TiO_2 composite membrane has illustrated a splendid separation ability for water-in-chloroform emulsion with flux ~20,000 L m^{-2} h^{-1} bar^{-1}, which was far beyond that of the other membranes with same thickness (Fig. S10). This result proved that the loading preparation of TiO_2 nanoparticles has an important influence on emulsion separation (Almessiere et al., 2020). Oppositely, if encountering with O/W emulsions, the continuous water phase will easily produce a stable barrier interface and make the emulsions change into metastable (Fig. 7H). Consequently, the water phase immediately penetrated

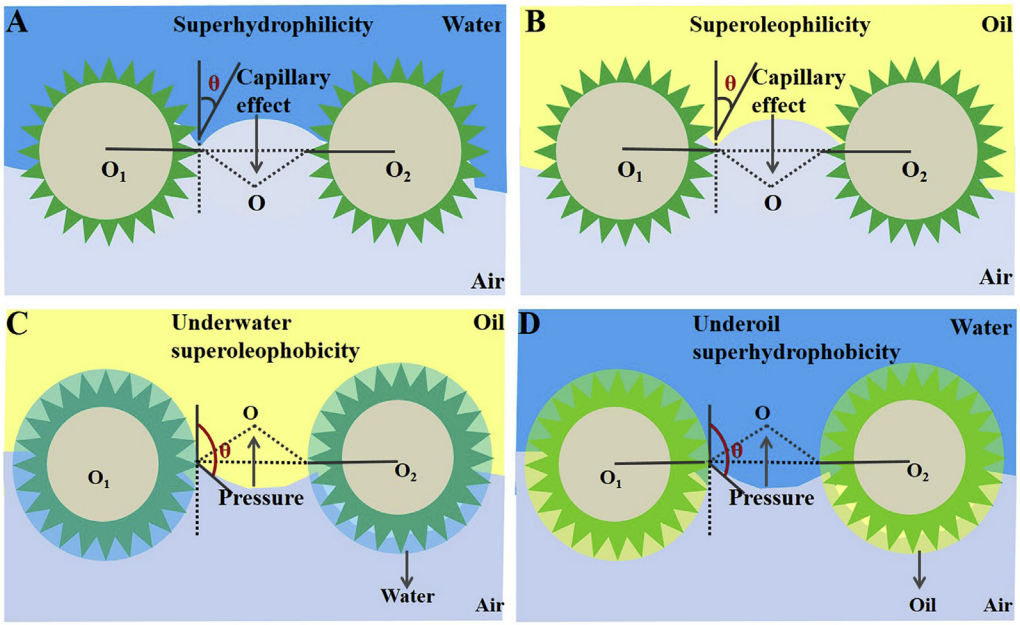

Fig. 6. Separation mechanism of CNTs/TiO_2 composite membrane for oil/water mixture. (A–B) The CNTs/TiO_2 composite membrane has shown superamphiphilicity in the air under the capillary effect. (C–D) Oil (water) cannot permeate the CNTs/TiO_2 composite membrane after being pre-treated with water (oil) because the CNTs/TiO_2 composite membrane can sustain some pressure ($\Delta P > 0$).

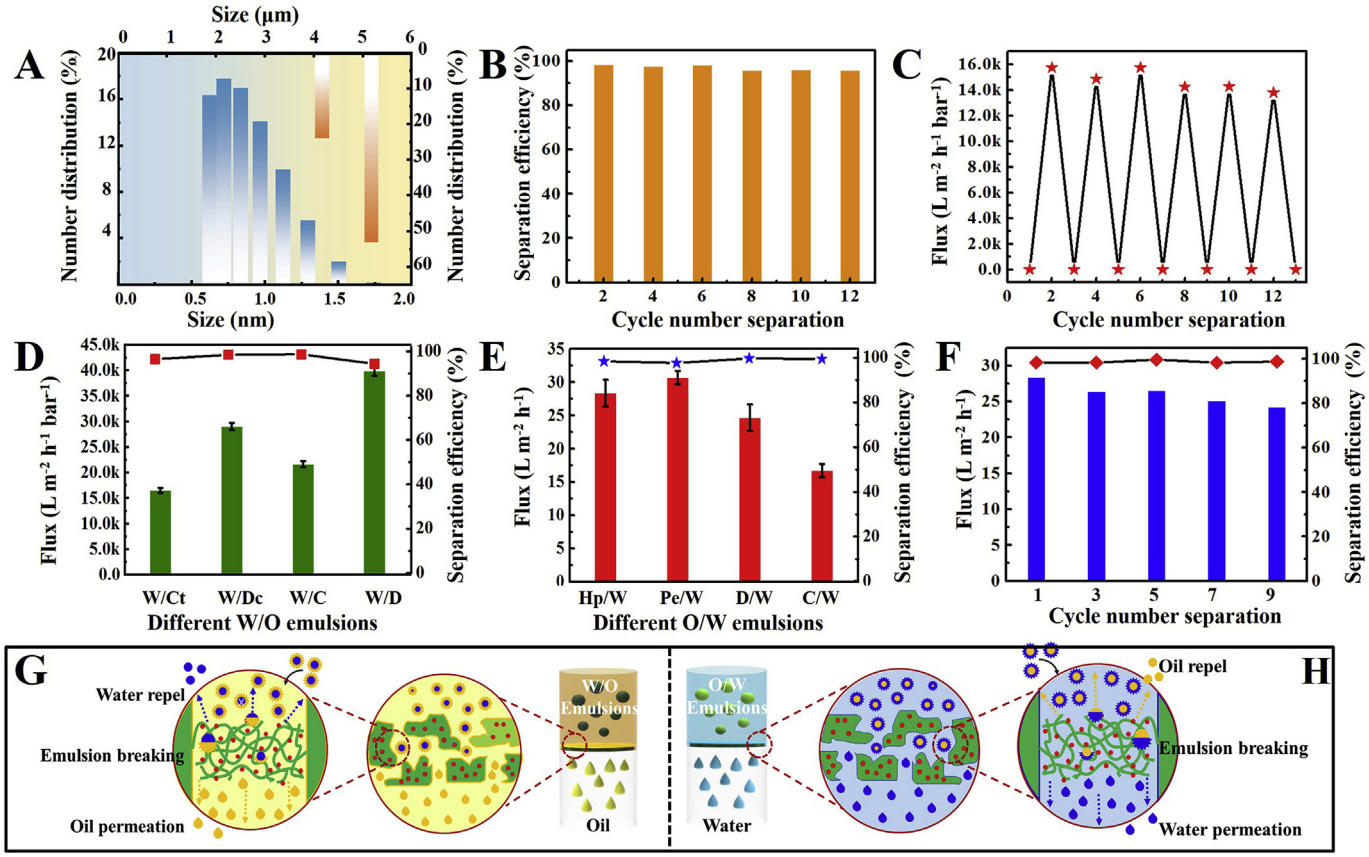

Fig. 7. (A) The DLS results for W/C emulsion (red) and (blue) filtration. The cyclic separation efficiency (B) and flux (C) of the CNTs/TiO_2 composite membrane for W/C emulsion. (D) The separation ability of various W/O emulsions passing through the CNTs/TiO_2 composite membrane. (E) The separation ability of this membrane for O/W emulsions. (F) The separation performance of the Hp/W emulsion passing through the CNTs/TiO_2 composite membrane versus the cyclic separation process. (G–H) Mechanism description of the CNTs/TiO_2 composite membrane for each type of emulsions separation, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

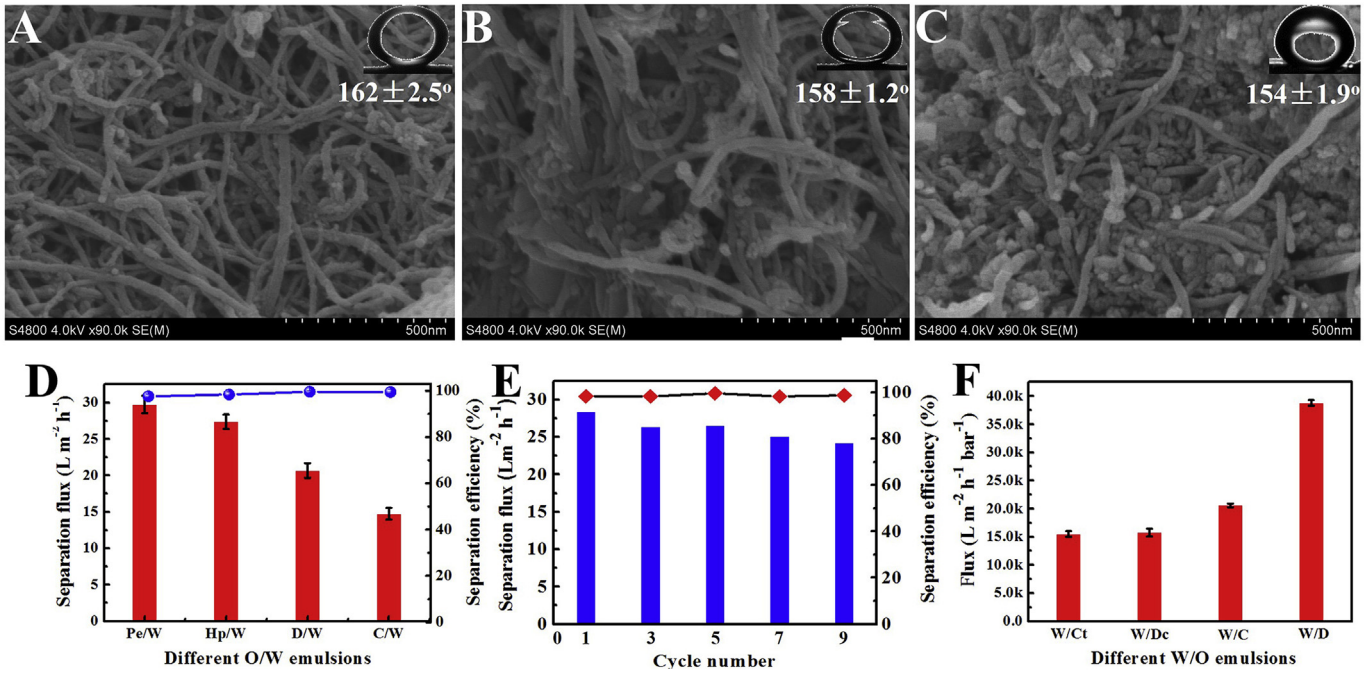

Fig. 8. (A–C)The SEM images of CNTs/TiO_2 composite membrane and their corresponding underwater oil contact angles after being treated in HCl, NaOH and NaCl for 24 h, respectively. (D) The separation efficiency and flux of various O/W emulsions passing through the CNTs/TiO_2 composite membrane after being treated with HCl (1 M) solution for 24 h. (E) The cyclic separation capacity of the Hp/W emulsion passing through the CNTs/TiO_2 composite membrane before being treated in HCl (1 M) solution for 24 h. (F) The flux of different W/O emulsions passing through the CNTs/TiO_2 composite membrane before being immerged in HCl (1 M) solution for 24 h.

through the membrane and yet the oil was obstructed. The optical microscopy and DLS results further proved its effective separation capability for O/W emulsions (Fig. S11). The permeability of the CNTs/TiO_2 composite membrane for O/W emulsions was also comprehensively investigated. As shown in Fig. 7E, the permeation flux for petroleum ether-in-water (Pe/W) emulsion with the lowest density of (0.64–0.66 g/mL) (Table S4) was higher than that of the other emulsions. These results were because the permeate flux for O/W emulsions is determined by the oil's density (Kango et al., 2013). The reliability of the CNTs/TiO_2 composite membrane was further assessed by taking cyclic experiments. As shown in Fig. 7F, there were substantially unchanged of separation flux and efficiency even after cyclic separation about Hp/W emulsion. From the above results, it was clear that the intelligent transport property has endowed the CNTs/TiO_2 composite membrane a medium for oil/water emulsion separation.

The stability of a filtration membrane under a harsh environment is essential for commercial applications (Liu et al., 2020; Zhang et al., 2018). The durability of the CNTs/TiO_2 composite membrane was further estimated by studying the structure and wettability before and after being treated with hydrochloric acid (1 M HCl) solution, sodium hydroxide (1 M NaOH) solution and sodium chloride (1 M NaCl) solution for 24 h. As shown in Fig. 8A–C, the CNTs/TiO_2 composite membrane has preserved its essential micro/nanostructure and wettability. Furthermore, the CNTs/TiO_2 composite membranes showed stable permeation flux and efficiency towards various O/W emulsions (Fig. 8D and E) and W/O emulsions (Fig. 8F). These results proved the CNTs/TiO_2 composite membrane has possessed with excellent environmental stability, which is propitious to separating various emulsions if treating actual wastewater.

4. Conclusions

In summary, we have displayed an easy and facile strategy to design a CNTs/TiO_2 composite membrane with selective wettability. Benefiting from its switchable transport property, this membrane was suitable for realizing the separation of sundry oil/water mixtures systems with splendid separation effectiveness, permeability, and recyclability no matter the solution is emulsified or not. It can maintain its separation efficiency above 99.1% even after ten cyclic separation. It is rather remarkable that this composite membrane has taken on prominent separation ability (flux ~ 40,000 L m^{-2} h^{-1} bar^{-1}, efficiency > 98.89%) for water-in-dichloromethane emulsion, which has surpassed most of the separation membranes reported to date. Furthermore, the CNTs/TiO_2 composite membrane has taken on predominant environmental stability even it was pre-treated with different corrosive aqueous solutions. This work has taken easy-to-prepare, anti-corrosion, multi-functionality and excellent separation performance into consideration, showing potential applications for task-oriented oily wastewater treatment.

Credit authorship contribution statement

Luke Yan: Methodology, Supervision. **Chaohui Liu:** Methodology, Data curation, Investigation. **Junyuan Xia:** Methodology, Data curation, Investigation. **Min Chao:** Methodology, Data curation, Investigation. **Wenqin Wang:** Data check. **Jincui Gu:** Writing-Reviewing and Editing, Supervision. **Tao Chen:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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