Superlyophobic anti-corrosive and self-cleaning titania robust mesh membrane with enhanced oil/water separation

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\textbf{A R T I C L E I N F O}

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\textbf{A B S T R A C T}

Oil/water separation becomes a research hotspot because of the frequent oil spill accidents. Although lots of separating membranes with super-wettability have been fabricated to separate oil or water from the mixtures, to separate both heavy (\(\rho_{\text{oil}} > \rho_{\text{water}}\)) and light (\(\rho_{\text{oil}} < \rho_{\text{water}}\)) oil/water mixtures with high efficiency and high flux is still a challenge, especially to obtain a membrane with mechanically robust nanostructures, and simultaneously anti-corrosive and self-cleaning ability. Herein, a novel titania nanostructured mesh membrane with superamphiphilicity in air, and dual superlyophobicity in liquid mediums were fabricated. Both high separation efficiency and flux of more than 99.2% and 16,954 L m\textsuperscript{-2} h\textsuperscript{-1} were obtained for both light and heavy oil/water mixtures. Importantly, the TiO\textsubscript{2} mesh membrane showed mechanically robust nanostructures and anti-corrosive ability, which can remain dual superlyophobicity, i.e., both underwater superoleophobicity and underoil superhydrophobicity and high oil-water separating behavior even after immersion in solutions of strong acid, basic, high salty, various organic solvents, and even after being abrased and adhered by pure sands and adhesive tape, respectively. Meanwhile, TiO\textsubscript{2} mesh membrane had shown photocatalytic decomposition of oil and organic molecules under UV irradiation, demonstrating unique self-cleaning and anti-fouling ability of the membranes. Given so many merits of these unique membranes, it is believed to these membranes have great potentials to be used in wastewater treatment and oil spill recovery.

1. Introduction

The frequently happened oil spill accidents cause increasingly environmental contamination [1–3]. With different interface interactions existing between oil and water, various membranes with special wettability performances have been designed to separate oil/water mixtures [4,5]. Generally, the existing separation membranes can be categorized into two categories. The first is for the membranes with superhydrophobicity/underwater superoleophobicity, considered as “water-removing” separation membranes including porous nitrocellulose membrane [6], hydrogel coated metal mesh [7], SiO\textsubscript{2} nanoparticles (NPs) and waterborne polyurethane (PU) coated stainless steel mesh [8], and titania coated metal mesh [9–11], which allow only water to penetrate through the membranes [12–20]. The other is those superhydrophobic/superoleophobic separation membranes, considered as “oil-removing” membranes, which allow oil to penetrate through the membranes [21–35], such as nanostructured layer steel mesh [36], superhydrophobic silica aerogels [37], polytetrafluoroethylene (PTFE) coated metal mesh [38], polydimethylsiloxane (PDMS) coated nanowire membrane [39], fly ash coated superhydrophobic textile [40] and zeolite-coated mesh [41]. Noticeably, all these materials can separate either light (\(\rho_{\text{oil}} < \rho_{\text{water}}\)) or heavy (\(\rho_{\text{oil}} > \rho_{\text{water}}\)) oil/water mixtures because of the barrier layer caused by the density difference between oil and water. Briefly, for these “water-removing” type materials, they are unsuitable for separating heavy oil/water mixture (\(\rho_{\text{oil}} > \rho_{\text{water}}\)), because oil will accumulate on the material surface,
forming the barrier layer and thus blocking the water permeation. Similarly, as to those “oil-removing” materials, separation of light oil/water mixture ($\rho_{\text{oil}} < \rho_{\text{water}}$) is unfavorable because water can sink down on the membrane surface, and thus prevents oil from permeating. Therefore, novel functional materials that can separate both heavy ($\rho_{\text{oil}} > \rho_{\text{water}}$) and light ($\rho_{\text{oil}} < \rho_{\text{water}}$) oil/water mixtures with high efficiency are still necessary.

Great efforts have been made to solve the aforementioned problems. For example, stimuli-responsive separating membranes that can switch between the superhydrophobicity/superoleophilicity and superhydrophilicity/underwater superoleophobicity have been reported to address the challenging separation of both heavy ($\rho_{\text{oil}} > \rho_{\text{water}}$) and light ($\rho_{\text{oil}} < \rho_{\text{water}}$) oil/water mixtures [42-47]. However, all these membranes need external stimuli including pH, temperature, solvent, etc., which are complex for operation and time-consuming. For example, Liu et al. realized both “oil-in-water” and “water-in-oil” emulsions separation based on the special dual superlyophobicity (underoil superhydrophobicity and underwater superoleophobicity) of the porous PVDF membranes [48]. Other membranes with similar wettability were also reported, such as ZnO/Co3O4 overlapped copper mesh membrane [49] and TiO2 nanoclusters coated copper mesh membranes [50]. All these only demonstrated the separation of oil-in-water and water-in-oil emulsions. However, for immiscible oil/water mixtures, these membranes would be unfavorable for practical applications because the pore sizes on these membranes are too small to realize high flux separation (small pore size is necessary for the separation of emulsions). To further overcome this imperfection, diatomite or corn cob powders (CCPs) coated stainless steel meshes were prepared by spraying the mixtures of diatomite/corn cob powders and waterborne polyurethane (PU), on which both heavy and light immiscible oil/water mixtures can be separated through “oil-removing” and “water-removing” separating processes [51,52]. Xiong et al [53] reported the separation of both heavy and light immiscible oil/water mixtures on a hierarchical ZnO nanosstructured nonwoven membrane with similar dual superlyophobicity. However, both good antifoaming ability and robust mechanical stability have not been demonstrated on these membranes for separating heavy oil/water mixtures. Du et al [54] reported a TiO2-coated stainless steel mesh membrane with dual superlyophobicity, on which both heavy and light immiscible oil/water mixtures can be separated. However, the membrane has not presented the anti-corrosive ability and robust nanostructure stability.

In this study, a novel nanostructured TiO2 mesh membrane was fabricated by a simple electrochemical anodization and heating process. Dual superlyophobicity, i.e., both underwater superoleophobicity and underoil superhydrophobicity were observed and used to efficiently separate both light and heavy oil/water mixtures. Light or heavy oil/water mixtures could be directly separated with an ultrahigh flux of more than 16,954 L m$^{-2}$ h$^{-1}$. Without any troublesome step such as pre-wet and external stimuli, the separation efficiencies are above 99.2% for all the used oil/water mixtures. Meanwhile, after physical abrasion and immersion into water solutions including strong alkali, acid, salty, various organic solvents, the nanostructures of TiO2 mesh membrane have not been damaged and the TiO2 mesh membrane still remains excellent separating property with high separation efficiencies above 99.2%, demonstrating mechanically robust nanostructure stability and anti-corrosive ability. Besides, TiO2 mesh membrane has shown photocatalytic decomposition of oil and organic molecules, which can decompose oil molecules under UV irradiation to make the fouled membrane recover to original wetting performances, showing unique self-cleaning and anti-fouling ability. Finally, the separation mechanism of nanostructured TiO2 mesh membrane was carefully analyzed by Young-Laplace equation.
2.6. Self-cleaning performance

The TiO$_2$ mesh fouled by a certain amount of diesel was irradiated with a 500 W mercury xenon lamp under controlled light intensity with a wavelength at 365 nm (CHF-XM-500 W, Beijing Chang Tuo technology co., Ltd). The change of the contact angle under UV irradiation was recorded to evaluate the self-cleaning performance of the TiO$_2$ mesh membrane. The following heating treatment was carried out in an oven at 150 °C for 1 h.

2.7. Characterization.

The microstructures of TiO$_2$ mesh membrane were observed on a scanning electron microscope (SEM, HITACHI, SU8010). The crystal phase of the membrane was identified through an X-ray diffractometer (XRD, X’Pert-Pro MRD, Philips). The contact angle (CA) was determined by using a contact angle meter (JC 2000D5, Shanghai Zhongchen Digital Technology Apparatus Co., Ltd) with constant water/oil droplet (ca. 4 μL). The CA was performed for five points at different positions, and an average value was adopted. For underwater oil and underoil water wettability measurements, the membrane was firstly fixed in a transparent container filled with water or oil, respectively. Then an oil droplet or water droplet was dripped upper or under the membrane to contact the membrane, depending on the density difference between oil and water. The adhesive force is determined by using a self-electro-mechanical balance system (Dataphysics DCAT 11, Germany). Briefly, an oil droplet (1, 2-dichloroethane, 4 μL) or a water droplet (4 μL) was suspended with needle tip and controlled to contact with the surface of the TiO$_2$ mesh membrane at a constant speed of 0.005 mm s$^{-1}$ and then to leave. The forces were recorded during the entire time.

3. Results and discussion

3.1. Surface morphology of nanostructured TiO$_2$ mesh membrane

Fig. 1a presents the SEM image of the original Ti mesh. It can be observed that the Ti wires (average diameter 105 μm, Fig. 1b) were wove together and formed “S” shaped pores. After the electrochemical anodization for a certain time and heating process (Figs. S1–S3), a number of nanoarrays grew vertically onto the Ti mesh substrate and the average diameter of Ti wire increased to about 123 μm (Fig. 1c and d). From the magnified images (Fig. 1e), the nanowires were observed to bundle together and form lots of nanopores with an average pore size of about 200 nm. The height and diameter of nanowires were about 18 μm and 20 nm, respectively (Figs. 1f and S4). The X-ray diffraction (XRD) result indicates that the obtained nanostructures are ascribed to the anatase TiO$_2$ (Fig. S5) [55], which is in agreement with the EDS result (Fig. S6). From the above, it can be concluded that the nanostructured anatase TiO$_2$ arrays can be produced on the Ti mesh substrate by a simple electrochemical anodization and heating process.

3.2. Wettability of nanostructured TiO$_2$ mesh membrane

In air, the as-fabricated membrane exhibited superhydrophilicity and superoleophilicity with both water contact angle (WCA) and oil contact angle (OCA) of almost 0° (Fig. 2a and b). After immersion in water or oil (n-hexane), the membrane shows superoleophilicity and superhydrophobicity with an OCA and WCA of about 160° and 158°, respectively, for clear observation (Fig. 4). Water filtrates form the membrane and oil is blocked (Fig. 4a and Video S1). However, for the heavy oil/water mixture, 1,2-dichloroethane/water mixture was used as an example, opposite phenomenon is observed that oil permeates through the membrane and water is blocked (Fig. 4b and Video S2). In addition, diesel, gasoline, petroleum ether, chloroform and water mixtures have also been separated successfully. These results indicate that light oil (ρ$_{\text{oil}} < \rho_{\text{water}}$) or heavy oil (ρ$_{\text{oil}} > \rho_{\text{water}}$)/water mixture were used to investigate the separating property of the membrane. For light oil (hexane)/water mixture, the water and oil are dyed with methylene blue and oil red O, respectively, for clear observation (Fig. 4). Water filtrates form the membrane and oil is blocked (Fig. 4a and Video S1).

3.3. Separation performances of nanostructured TiO$_2$ mesh membrane

The membrane with such a special superwetting performance is reported to be able to separate oil/water mixtures [56]. In order to evaluate the separating ability of the TiO$_2$ mesh membranes, some proof-of-concept studies have been conducted. As mentioned in introduction, the traditional separating membranes with superhydrophobicity/superoleophilicity and superhydrophilicity/underwater superoleophobicity can separate either light (ρ$_{\text{oil}} < \rho_{\text{water}}$) or heavy (ρ$_{\text{oil}} > \rho_{\text{water}}$) oil/water mixtures, because the barrier layer caused by the density difference between oil and water often arises during the separation process. Both heavy (ρ$_{\text{oil}} > \rho_{\text{water}}$) and light (ρ$_{\text{oil}} < \rho_{\text{water}}$) oil/water mixture were used to investigate the separating property of the membrane. For light oil (hexane)/water mixture, the water and oil are dyed with methylene blue and oil red O, respectively, for clear observation (Fig. 4). Water filtrates form the membrane and oil is blocked (Fig. 4a and Video S1). However, for the heavy oil/water mixture, 1,2-dichloroethane/water mixture was used as an example, opposite phenomenon is observed that oil permeates through the membrane and water is blocked (Fig. 4b and Video S2). In addition, diesel, gasoline, petroleum ether, chloroform and water mixtures have also been separated successfully. These results indicate that light oil (ρ$_{\text{oil}} < \rho_{\text{water}}$) or heavy oil (ρ$_{\text{oil}} > \rho_{\text{water}}$)/water mixtures could be separated under gravity-driven action, achieving “water-removing” or “oil-removing” type on our membrane.

Supplementary Video 1.
Fig. 1. (a) and (b) SEM images of pure Ti mesh substrate at low and high magnifications, respectively. (c) and (d) SEM images of TiO$_2$ mesh membrane at low and high magnifications, respectively. (e) SEM images of the TiO$_2$ nanostructure. (f) The cross-sectional SEM image of TiO$_2$ nanostructures.
Fig. 2. (a) and (b) A water droplet (4 μL) and an oil droplet (1, 2-dichloroethane, 4 μL) on the TiO₂ mesh membrane in air with a CA of almost 0°; (c) and (d) Underwater oil droplet (1, 2-dichloroethane) and underoil water droplet on the membrane with OCA and WCA of about 160° and 158°, respectively; (e) and (f) Photographs of the dynamic underwater oil-adhesion and underoil water-adhesion measurement on the membrane. An oil droplet (1, 2-dichloroethane, 4 μL) (e) or a water droplet (4 μL) (f) was used as the detecting probe to contact the membrane and then leave. It can be seen that the mesh membrane exhibited an ultralow affinity to oil and water in water and oil, respectively. (g) and (h) Force-distance curves recorded before and after the underwater oil droplet (g) and underoil water droplet (h) came into contact with the membrane, respectively.
Fig. 3. Statistic of OCA for various oils in water and WCA in various oils, respectively.

Fig. 4. Oil/water separation processes: (a) for light oil/water mixture ($\rho_{\text{oil}} < \rho_{\text{water}}$), water would sink spontaneously due to the higher density (left Fig.) When the valve is opened, water can permeate the membrane and the following oil be retained (right Fig.) (b) For heavy oil/water mixture ($\rho_{\text{oil}} > \rho_{\text{water}}$), the oil would pass through the membrane and water was blocked. The water is dyed with methylene blue and oil is dyed with oil red for clear observation.

Fig. 5. (a) The separation efficiency and flux of TiO$_2$ mesh membrane for different light and heavy oil/water mixtures (b) Experimental values of intrusion pressures for various oils (water-removing type) and water (oil-removing type).
Supplementary Video 2. To assess the separation ability for the TiO₂ mesh membrane, the separation efficiencies were first investigated. According to Eq. (1), the separation efficiencies were calculated for all used oil/water mixtures, which are higher than 99.4% (Fig. 5a), demonstrating a good separating ability of our membrane. Besides the separating efficiency, the liquid flux (F) is also measured, which is calculated by using Eq. (2) [10].

\[ F = \frac{V}{St} \]  

where \( V \) is the water or oil filtration volume, \( S \) is the membrane area and \( t \) is the permeation time of liquids with a fixed volume. The results show that all liquid fluxes were higher than 16,954 L m\(^{-2}\)h\(^{-1}\) (Fig. 5a), meaning that our membrane can realize fast separation. Furthermore, the intrusion pressure (an important performance during separation process) of the membrane was defined as the maximum height of liquid mediums (hexane, gasoline, petroleum ether, diesel, 1, 2-dichloroethane and chloroform) and was also investigated. For “water-removing” separation type, various oil intrusion pressures are examined, while for “oil-removing” separation type, water intrusion pressures are determined. Accordingly, the experimental intrusion pressures (\( P_{\text{exp}} \)) can be obtained by using Eq. (3) [7].

\[ P_{\text{exp}} = \rho gh_{\text{max}} \]  

where \( P_{\text{exp}} \) is the experimental value, \( \rho \) is liquid density, \( g \) is gravity acceleration and \( h_{\text{max}} \) is liquid maximum height. The greater the value of intrusion pressure, the better the stability of the TiO₂ mesh membrane is. Fig. 5b indicates that the intrusion pressures for all liquids are higher than 0.85 kPa, showing that TiO₂ mesh membrane possesses a good stability.

3.4. The anti-corrosive, mechanical stability and self-cleaning performances

For practical application, the anti-corrosive property of the membrane is of vital importance. Generally, inorganic separating materials such as oxides and metals are unstable in water solutions with strong acid or basic [8,49], while organic membranes can be easily damaged by organic solvents (such as 1, 2-dichloromethane, chloroform and diesel used in this work) [37,38], which seriously affect their realistic applications. Noticeably, the as-prepared TiO₂ mesh membranes possess a unique anti-corrosive property. In order to estimate its anti-corrosive ability, the membrane is immersed in aqueous solutions containing 1 M HCl, 10 wt% NaCl, 1 M NaOH, and various oils used here (1, 2-dichloromethane, chloroform and diesel), respectively for 24 h. The microstructures of the membranes had no apparent variation (Figs. S7 and S8), and then the underwater oil and underoil water wetting performances were tested (for samples immersed in oils, treated by UV irradiation and heating process, we will discuss this in the later section). As shown in Fig. 6a and b, it can be seen that after 24-hour immersion, the underwater superoleophobicity and underoil superhydrophobicity can still be observed with underwater OCA and underoil WCA of 154° and 152°, respectively. Meanwhile, the separation efficiencies are still higher than 99.2%, showing that the membrane possesses a better anti-corrosive performance.

In addition to the anti-corrosive property, the mechanical stability of the surface microstructure is also important, since a lot of external actions such as friction and pressing can also result in the damage of surface microstructures, which can often lead to the loss of separating function of the membrane and is difficult to be avoided in realistic conditions. Herein, to demonstrate the good mechanical stability, the experiments about the impact of flowing sands and the adhering of adhesive tape were carried out. The membrane’s microstructures have no apparent variation after these experiments, and the underwater superoleophobicity and underoil superhydrophobicity can still be observed, respectively (Fig. S9), indicating a good mechanical stability.

Another problem facing separating materials is the fouling and is often inevitable during the practical applications. As is well known,
after continuous separation of complex oily wastewater, the membrane might be fouled by some oils or organic molecules, and then lose its original surface wettability and separating ability. With a strong photocatalytic degradation activity of anatase TiO$_2$ [57], the membrane is expected to have a special self-cleaning property. To assess the self-cleaning performance, TiO$_2$ mesh membrane has been fouled arbitrarily with a certain amount of diesel. After fouling, the wettability of the membrane changes into hydrophobicity in air, underwater oleophobicity and underoil superhydrophobicity (Fig. 7a–c). Noticeably, such an oil-fouled membrane could not separate light oil/water mixture, indicating that the oil fouling has seriously affected the separating property of the membrane. After a simple UV irradiation and heating process, it is worth to note that the wetting performance of the fouled TiO$_2$ mesh membrane can restore to its original superhydrophilicity and dual superlyophobicity (Fig. 7d–f), demonstrating that the obtained membrane has a particular self-cleaning property (from here, it would be easy to understand that why the membrane needs to be irradiated by UV and heating at 150°C for 1 h as mentioned in Fig. 6). As shown in Fig. 7g, it is seen that the WCA of the membrane gradually decreases with the increase of UV illumination time. After UV illumination for 240 min, the membrane shows superhydrophilicity with a WCA of almost 0°, which is ascribed to the direct decomposition of diesel molecules by photo-induced holes and hydroxyl radicals with strong oxidation [58].

3.5. Stability of separation performance

To further investigate the recyclability of nanostructured TiO$_2$ mesh membrane, the separation efficiency over water/oil mixtures with the volume ratio of 1:1 was repeated for 10 times. The overall separation efficiencies are shown in Fig. 8. The separation efficiencies of the nanostructured TiO$_2$ mesh membrane for “water-removing” type (hexane
and water mixture, $\rho_{\text{oil}} < \rho_{\text{water}}$) and “oil-removing” type (1, 2-dichloroethane and water mixture, $\rho_{\text{oil}} > \rho_{\text{water}}$) were higher than 99.4% and 99.2%, respectively (Fig. 5a and b). Based on the switchable ability between underwater superoleophobicity and underwater superhydrophilicity, the nanostructured TiO$_2$ mesh membrane can also be used to alternately separate light oil or heavy oil/water mixture. After 10 alternate cycles, the separation efficiency still remained higher than 99.2% (Fig. 5c). These results demonstrate that our membrane has a good recyclability.

### 3.6. Separation mechanism of nanostructured TiO$_2$ mesh membrane

From the above, it can be found that the superamphiphilicity and dual superlyophobicity endow the membrane with special separating ability. For a better understanding of the phenomena, the inner mechanism that affects the wettability of the membrane was carefully analyzed. TiO$_2$ is known as a kind of hydrophilic and oleophilic material [59]. After introducing nanostructures, the capillary effect would enhance the surface wettability according to Wenzel Equation ($\cos \theta = r \cos \theta$) [60]. Thus, the membrane shows superhydrophilicity and superoleophobicity in air (Fig. 2a and b). When such a superhydrophilic membrane was placed in water, water could enter the nanostructures easily. When an oil droplet contacts the membrane, a new solid/water/oil interface can be formed (Fig. S10a). The high OCA can be illustrated by Eq. (4) [61].

$$\cos \theta'_{\text{oil}} = f \cos \theta_{\text{oil}} + f - 1$$

where $\theta'_{\text{oil}}$ and $\theta_{\text{oil}}$ are the OCAs on the nanostructured membrane and flat substrate, respectively, $f$ is the contact area fraction. 1, 2-dichloroethane is chosen as the measured oil droplet, $\theta'_{\text{oil}} = 160 \pm 1^\circ$ (Fig. 2a), $\theta_{\text{oil}} = 117 \pm 1^\circ$ (Fig. S10b) and $f = 0.11$, showing that the contact area of oil/water interface is 89%. Thus, underwater superoleophobic and low adhesive force can be viewed (Fig. 2g). Similarly, as the membrane is placed into oil, a water droplet also resides in the composite state, and the solid/water contact area is as low as 16.5%. Therefore, our membrane also shows a low adhesive underwater superhydrophobicity (Fig. 2h, Fig. S10a, c and discussion).

To understand the separation process clearly, the water and oil wetting process was modelled in Fig. 9. As reported, $AP$ is needed to be overcome before liquid wetting the pores because the advancing contact angle ($\theta_A$) must be surpassed, which can be explained by Eq. (5) [62].

$$P = \frac{2\gamma}{R} = -l\gamma(\cos \theta_A)/A$$

where $\gamma$ is the interfacial tension, $l$ is the perimeter of the pores, $R$ is the radius of the meniscus, $\theta_A$ is the advancing contact angle, and $A$ is the cross-sectional area of the pore. From Eq. (5), it can be easily understood that for the $\theta_A > 90^\circ$, the membrane could sustain a degree of pressure because $\Delta P > 0$. On the contrary, the membrane cannot withstand any pressure for the $\theta_A < 90^\circ$, and liquids can permeate through the membrane spontaneously because $\Delta P < 0$. Fig. 2a and b show that in air, the membrane is superamphiphilicity with a $\theta_A$ of almost $0^\circ$, and the membrane cannot support any pressure since $\Delta P < 0$ (Fig. 9a and c). Therefore, as shown in Fig. 4, under gravity-driven action, the water and oil can permeate the membrane spontaneously as they first contact the membrane. What needs to be stressed is that, during the permeation process, some water or oil could be trapped in nanopores. When the following oil or water contacts the membrane, it would reside in the composite wetting states as discussed above. Accordingly, the underwater superoleophobicity and underoil superhydrophobicity can be observed (Fig. 2c and d). Under these conditions, $\theta_A$ is certainly larger than $90^\circ$, showing that the TiO$_2$ mesh membrane could support a degree of pressure because $\Delta P > 0$ (Fig. 9b and d). Therefore, after the permeation of water or oil, the following oil or water would be retained, Fig. 4, thus, the separation of heavy or light oil/water mixtures is successfully realized by using the TiO$_2$ mesh membrane.

### 3.7. The performance comparison of reported separation membranes with special dual superlyophobicity

As shown in Table 1, these separation membranes show special dual superlyophobicity, i.e., both underwater superoleophobicity and underoil superhydrophobicity, and high separating efficiency above 98.0%. However, based on the special dual superlyophobicity, TiO$_2$...
their practical applications because the pore sizes on these membranes are too small to realize high flux separation (small pore size is necessary for the separation of emulsions). To further overcome this imperfection, a diatomite-coated stainless steel mesh [51] and ZnO nanostructured PET nonwoven fabrics [53] have successively reported, which were used to successfully separate both heavy and light immiscible oil/water mixtures on a single membrane with high flux of 25,200 L m$^{-2}$ h$^{-1}$ and 6900 L m$^{-2}$ h$^{-1}$, respectively. However, the self-cleaning property and good antifouling ability have not been demonstrated on these membranes for separating heavy oil/water mixtures due to preferential penetration of heavy oil. And then, TiO$_2$-coated stainless steel mesh membrane [54] has been further reported, which show high flux of more than 7281 L m$^{-2}$ h$^{-1}$ and self-cleaning property due to TiO$_2$ photocatalytic activity. However, the separation membrane has not presented the anti-corrosive ability and robust nanostructure stability. Therefore, in this work, a novel titania nanostructural mesh membrane with dual superlyophobicity were fabricated to successfully separate both heavy (ρ$_{\text{oil}} >$ ρ$_{\text{water}}$) and light (ρ$_{\text{oil}} <$ ρ$_{\text{water}}$) oil/water mixtures with high separation efficiency and higher flux of more than 99.2% and 16,954 L m$^{-2}$ h$^{-1}$, respectively. Most importantly, TiO$_2$ nanostructured mesh membrane can simultaneously possess anti-corrosive ability, self-cleaning property and robust nanostructure stability. Given so many merits of the unique membrane, it could be believed to be potentially used in wastewater treatment and oil spill recovery.

### 4. Conclusion

In short, TiO$_2$ mesh membrane has been fabricated by electrochemical anodizing and heating processes, which shows super-amphiphilicity in air and dual super-lyophobicity. Based on the membrane with such special wettability of dual superlyophobicity, i.e., both underwater superoleophobicity and underoil superhydrophobicity, both light (ρ$_{\text{oil}} <$ ρ$_{\text{water}}$) and heavy (ρ$_{\text{oil}} >$ ρ$_{\text{water}}$) oil/water mixtures could be highly efficiently separated (separation efficiency higher than 99.2%). Meanwhile, the membrane also demonstrates good mechanical stability, anti-corrosive and self-cleaning ability, and remains excellent

![Fig. 9](image-url). Schematic illustration of the liquid-wetting models: TiO$_2$ mesh membrane shows superhydrophilicity (a) and superoleophilicity (c) in air and cannot sustain any pressure because of $\Delta P < 0$, thus water or oil can permeate through the membrane spontaneously. (b) and (d) water or oil first permeates through the membrane and the nanostructures have been occupied by water or oil, showing underwater superoleophobicity or underoil superhydrophobicity. Some water or oils can be supported on the TiO$_2$ mesh membrane because $\Delta P > 0$. Thus, the separation of all kinds of oil/water mixtures can be achieved regardless of density difference.

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<th>Table 1</th>
<th>The performance comparison of reported separation membranes with dual superlyophobicity.</th>
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<td>Separation membrane</td>
<td>Separation object</td>
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<tr>
<td>Lin et al. [50]</td>
<td>Oil-in-water emulsion</td>
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<td>TiO$_2$ nanoclusters coated copper mesh membrane</td>
<td>Water-in-oil emulsion</td>
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<td>Li et al. [51]</td>
<td>Light oil/water mixture</td>
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<td>A diatomite coated coated stainless steel mesh</td>
<td>Heavy oil/water mixture</td>
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<td>Xiong et al. [52]</td>
<td>Light oil/water mixture</td>
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<td>ZnO nanostructured PET nonwoven fabrics</td>
<td>Heavy oil/water mixture</td>
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<td>Du et al. [53]</td>
<td>Light oil/water mixture</td>
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<td>TiO$_2$-coated stainless steel mesh membrane</td>
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nanoclusters coated copper mesh membrane [50] were only used to separate “oil-in-water” and “water-in-oil” emulsions with highest flux of 9860 L m$^{-2}$ h$^{-1}$ and 750 L m$^{-2}$ h$^{-1}$, respectively, which would be unfavorable for immiscible oil/water mixtures and significantly limit
separating property even after immersion into water solutions including strong alkali, acid, salty, various organic solvents, and even physical abrasion. Considering high separation efficiency, anti-corrosion, and self-cleaning of the membrane, the membranes can be potentially applied in wastewater disposing, microfluidic device, and oil spill recovery.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jseppur.2018.03.002.

References

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