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Durable superhydrophobic and superoleophilic electrospun nanofibrous membrane for oil-water emulsion separation



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G R A P H I C A L A B S T R A C T

The preparation of superhydrophobic and superoleophilic PI-based nanofibrous membrane for oil-water separation.



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ABSTRACT

Marine pollution and industrial wastewater have caused serious environmental pollution, thereby resulting into an alarming damage to public health in the past decades, hence the high demand for, cost effective, energy-efficient oil-water separation technologies for the removal of oil contaminants from such water. Herein, we report a facile method to fabricate superhydrophobic/superoleophilic membrane by immersing a polyimide (PI)-based nanofibrous membrane into a water/ethanol/ammonia/dopamine mixture, followed by modification with 1H, 1H, 2H, 2H-perfluorodecanethiol (PFDT). The PI-based membrane exhibited water contact angle (WCA) above 153°, while the oil contact angle (OCA) approached 0°, thereby promoting an outstanding chemical stability which sustained its superhydrophobicity when immersed in aqueous solutions at different pH values. Additionally, the PI-based membrane possesses ultrahigh flux, high separation efficiency and good reusability in oil-water separation. The aforementioned properties, as well as the easily scale-up preparation process ensure that this promising

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1. Introduction

The separation of oil from oily wastewater is a particularly important pursuit due to the ever-increasing global oil pollution [1], hence an urgent need for scientists to develop cost-effective oil-water separation methods to separate oil-water mixtures. However, several previously reported strategies including gravity separation [2], adsorption [3], skimming [4], solved air flotation [5], centrifugation [6], biological treatments [7] and electro coalescence [8], which are widely used for separation of oil/water mixtures, consume a great deal of energy during the separation process, with low separation efficiency, easy corrosion and repeated pollution seems inevitable [9–11]. Therefore, the need for the development of highly efficient, low energy consuming, and cost-effective technologies to separate oil/water mixtures. Membrane separation techniques have recently been demonstrated to be a promising strategy for the separation of oil/water mixture, with several studies reporting the superiority of different kinds of membranes in the process of oil-water separation when compared to the current conventional technologies [1,2]. Electrospinning [10,12–15], a versatile method, has emerged to creating nonwoven mats with high efficiency, environmental protection, energy conservation, as well as simple and easy-to-control process, and can generate continuous fibers with different dimeter and varied morphologies as well as highly interconnected uniform size porous membrane structure [16]. So far, the electrospun nanofiber membranes have been used for water treatment in a variety of applications including nanofiltration, ultrafiltration and forward osmosis [17-19]. The large surface/volume ratio [15], high interconnected pore structures, high porosity and controllable pore sizes of the electrospun membrane, make it to possess high permeability in oil-water separation, which does not only improves the separation efficiency but also reduces the energy consumption of the process [20–23]. However, the most of the electrospun fibrous membranes exhibit poor mechanical strength due to the overlap and separation of individual fibers. Polyimide based polymers are considered to be one of the most important super-engineered materials due to their enhanced mechanical properties, heatand corrosion resistance, chemical and hydraulic stability.

Super wetting materials have received considerable attention in recent years. Designing materials with special wettability, is a versatile method to achieve oil/water separation by either selective absorption or filtration of oils/water from mixtures. However, the materials with super-wettability usually have poor mechanical stability, as they easily lose their superhydrophobicity in harsh conditions. Previously, we have reported a superhydrophobic and superoleophilic F-PBZ/SNPs/CA-PI nanofibers membrane via a facile combination of coaxial electrospun cellulose-acetate (CA)-PI nanofibers and a novel in-situ polymerized F-PBZ functional layer containing silica nanoparticles (SNPs). The as-prepared membranes could effectively separate various kinds of oil-water mixtures via filtration [9]. In another work, Zhang et al., [24] developed intelligent materials with switchable oil/water wettability in aqueous media. Using a copolymer-grafting strategy, textiles and sponge materials were functionalized by a block copolymer, comprising pH-responsive poly(2-vinylpyridine) and oleophilic/ hydrophobic polydimethylsiloxane blocks (i.e., P2VP-b-PDMS) to achieve the functionality. The functionalized materials with reversible switching between superoleophilicity and superoleophobicity can be used for highly controllable oil/water separation process. These studies, therefore provided a new route to the designing and fabrication of functionalized membranes for filtration and separation applications.

Dopamine, a typical catecholamine, which contains catechol moieties of 3,4-dihydroxy-L-phenylalanine (DOPA) and amino groups of lysine, can self-polymerize in alkaline solution, forming a thin polydopamine (PDA) layer which can spontaneously deposit onto various material surfaces due to the strong



Scheme 1. Schematic illustration of the superhydrophobic modification of electrospun PI nanofibrous membranes.

covalent/noncovalent interactions between catechol moieties and substrates [25–28]. Mostly, the PDA have been broadly explored as the intermediate platform for further versatile surface functionalization to achieving satisfactory separation properties. In this present work, we designed hierarchical structure by simply immersing the PI-based fibrous membrane into a mixture of water/ethanol/ammonia/dopamine at ambient temperature. The roughness of the modified PI nanofibrous membranes can be adjusted by the addition of ammonia, hence, their surface wettability is under control. Followed by the modification with 1H, 1H, 2H, 2H-perfluorodecanethiol(PFDT), the resultant PFDT/PDA/PI nanofibrous membranes exhibits remarkably stable superhydrophobicity, even after extreme pH, high temperature and rigorous abrasion treatment. This work provides a new strategy to design and fabricate a membrane with hierarchical surface for oil-water separation, in which no special chemicals or extra nanoparticles are required. thereby making it much simpler, time-saving, cost-effective process, in addition to the products being environmentally friendly with minimal negative effect on the surroundings after use (Scheme 1). This indicates the attractive potential applications in practical oil-water separation and oil spill cleanup process.

2. Experimental section

2.1. Materials and reagents

Dopamine hydrochloride (AR, 98%), p-phenylenediamine (PDA, 97%), 1H, 1H, 2H, 2H-perfluorodecanethiol (PFDT, 97%), hexadecyltrimethylammonium bromide (CTAB, 99%), methylene blue (AR, 98.5%), Sudan III (HPLC, ≥96%), *n*-hexadecane (AR, 98%), aqueous ammonia (AR, 25-28%), olive oil (CP), sunflower seed oil (99%), kerosene (98%) and flax seed oil (99%) were all purchased from Aladdin (Shanghai), while 3,3,4,4-Biphenyl tetracarboxylic dianhydride (BPDA, 98%) was obtained from TCI (Shanghai). Chloroform (AR, 99%), 1, 2-dichloroethane (AR, 99%), petroleum ether (AR, bp 60–90 °C), toluene (AR, 99.5%), *n*-hexane (AR, 97%), anhydrous ethanol (AR, 99.7%), acetone (AR, 99.5%), dichloromethane (AR, 99.5%), N, N-Dimethylacetamide (DMAc) (AR, 99.5%), bromobenzene (AR, 98%) and tetrachloromethane (AR, 99.5%) were obtained from Nanjing Chemical Reagents. However, both BPDA and PDA were sublimated before use. Unless stated otherwise, all chemicals and reagents were used as received from the supplier without further purification.

2.2. Synthesis of polyamide acid (PAA)

PAA was synthesized according as reported by Ma et al. [9]. Briefly, solid PDA (1.0814 g, 0.01 mol) and BPDA (2.9422 g, 0.01 mol) were added slowly to DMAc (40 mL), followed by vigorous mechanical stirring under nitrogen, with the internal temperature maintained at -5 °C. The solution was made to stir overnight.

2.3. Fabrication of Polyimide (PI) nanofibrous membrane

The process of electrospinning was performed according to previous studies [9]. A 3 wt% precursor solution containing 0.3 g PAA and 10 g DMAc was placed into a 1 mL syringe with a metallic needle tip. A high voltage power supply was used as the source of electric field, while a rotational collector (1500 rpm) was connected to collect the nanofibers. The optimal electrospinning parameters were as follows: feed rate = $1.0 \text{ mL} \cdot \text{h}^{-1}$, applied spinning voltage = 15 kV, the distance between the needle tip to the collector = 10 cm. Scheme 1shows a schematic diagram for the utilized apparatus. Finally, the as-prepared PAA nanofibrous membrane was thermally converted into PI membranes through imidization.

2.4. Fabrication of the PFDT/PDA coating solution

A 0.40 mL 28–30 wt% ammonia aqueous solution (NH₄OH) was added to 100 mL of ethanol/H₂O mixture (30 vol% ethanol), under a mild stirring for 30 min, followed by the addition of 0.2 g dopamine hydrochloride to the mixture while stirring. The stirring continued overnight, after which 1 mL of 2% volume of PFDT (dissolved in methanol) was subsequently added to the resulting browncolored solution. The above mixed solution was further vigorously stirred for another 1 h to obtain the desired coating solution.

2.5. Preparation of the PFDT/PDA/PI membranes

Firstly, the electrospun PI membranes were cleaned with acetone and water to remove any surface impurities, after which they were dipped into the PFDT/PDA coating solution for 12 h. The dipped membranes were thereafter removed from the solution and dried at ambient temperature, followed by oven-drying at 60 °C for 20 min. Finally, the PFDT/PDA modified membranes were heated at 120 °C in a vacuum oven for 3 h to enable full vaporization of PFDT onto the surface of the membrane.

2.6. Free oil-water mixture separation experiments

A home-made device was fabricated for the separation of the free oil-water mixture. The device consists of a flange, retort stands, two glass tubes, beakers and the as-prepared membranes. The as-prepared membranes were fixed between two 20 mm-diameter glass tubes by the flange. Before the oil-water mixture (1/1, v/v) separation process, the as-prepared membranes were pre-wetted with oil, after which a mixture of oil (DCM, dyed with Sudan III) and water (dyed with methylene blue) prepared in a bot-tle under ultrasonication, was poured onto the membrane through the upper tube, and the retained water and permeated oil were collected with the glass tube and the beaker, respectively.

2.7. Surfactant-stabilized water-in-oil emulsions separation experiments

Four kinds of water-in-oil emulsions were prepared in this experiment. 1 mL water added to 50 mL toluene, hexane, chloroform and kerosene, respectively, (containing 0.1 wt% span 80) were vigorously stirred for 12 h, followed by treatment using ultrasonic processor (SCIENTZ, 40 kHz) for 5 min to produce a milky solution. The separation apparatus was the same as the free oil-water mixture separation.

2.8. Instrumentations and characterization

The electrospun membranes were prepared using the commercially available spinning instruments (Future, FM1206, Beijing, China). The composition of the membrane was recorded using a Nicolet 7000 FT-IR spectroscopy, while the surface morphology of the sample was observed using a scanning electron microscope (SEM, S-4800, Hitachi, Ltd., Japan). Furthermore, the mechanical properties of the membrane were determined using a universal material testing machine (Sans, UTM6502, Shenzhen, China), with the measurements being conducted at 25 °C, while the surface hydrophobic/oleophobic properties of the membranes were analyzed with a JC2000D1instrument (Zhong Chen, Shanghai, China), in which three different regions of each surface were measured. Furthermore, the atomic force microscope (AFM) (Dimension Edge, Bruker, Germany) images were acquired using tapping mode An optical microscope (E200, Nikon, Japan) was employed to observe the emulsions and filtrates, while the emulsion droplet size distribution was measured on a Zetasizer Nano ZS (Malvern, Worcestershire, UK), with all measurements performed three times (n = 3). The chemical composition of the membrane was measured by an Axis Ultra spectrometer using *Al K* α radiation (XPS, Kratos Analytical Ltd., UK). Thermogravimetric analysis (TGA) analysis were performed for the powder samples in Al₂O₃ crucibles at a heating rate of 10 °C/min under dynamic nitrogen flow using a TA 50 instrument (TA, USA), while the surface properties of the membranes were studied by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) model via nitrogen adsorption and desorption measurements isotherms performed using an Autosorb-1 MP sorption instrument (Quantachrome, USA). The X-ray powder diffraction (XRD) analysis was conducted using an Ultima IV, Rigaku (Japan) at a scanning rate of 2°/min. Finally, Total organic carbon analyzer (Torch, USA) was used to measure oil concentration.

3. Results and discussion

3.1. Chemical characterization of the PFDT/PDA/PI fibrous membranes

The PI nanofibrous membrane is chosen as the skeleton of separation because of its robustness, cost-effective and wider availability, all of which are very desirable features for a highperformance filtration. Fig. 1a exhibits the SEM image of the untreated, smooth PI membrane samples with average fiber diameter of about 300 nm. After the PDA modification, the skeleton of the PI nanofibers membrane became relatively rough (Fig. 1b). The PDA with uniform layer covered the PI nanofibers surface, thereby forming rough micro-/nano-scale hierarchical structure. As previously reported, the surface wettability of a material is decided by both their geometrical structure and chemical composition [29,30]. In addition, the PDA coating and hydrophobic 1H, 1H, 2H, 2H-perfluorodecanethiol modification do not have any damaging effect on the PI nanofibrous membrane (Fig. 1c), as the modifications are expected to provide low energy surface and an increase in surface hydrophobicity.

Significantly, the as-prepared membranes were also characterized by various surface analytical techniques. FTIR spectra of pristine PI, PDA/PI and PFDT/PDA/PI membranes are shown in Fig. 2a. The peaks at 1770, 1720, and 1370 cm^{-1} were attributed to the -CONH, -COOH and C-N stretching vibrations, respectively. After the self-polymerization of dopamine onto the PI nanofiber surface, three additional peaks appeared in the spectrum of the membrane at 1615, 1057 and 1271 cm⁻¹, respectively, which were consistent with the main vibrational modes of C=N, OH and C-N- of PDA, indicating the formation of thin PDA layer on the PI nanofiber surface. In making a comparison between the infrared spectra of PDA modified- and PFDT/PDA modified PI membranes, the appearance of peaks located at 1271 and 1160 cm⁻¹ were attributed to C–S–C and -C-F, respectively, indicating the successful functionalization of the PI nanofiber with PFDT/PDA. The surface chemical composition of the as-prepared membrane was further verified. As shown in Fig. 2b, C1s (285 eV), N1s (399 eV) and O1s (532 eV) were clearly visible in the spectra of PDA/PI. However, after the modification by PFDT/PDA, a new peak, F1s (687 eV), was observed in addition to the C1s, O1s and N1s peaks. The characteristic XPS peaks intensities of PDA/PI displayed a significant increase after the reaction functionalization with PFDT/PDA [31]. Furthermore, the treated membranes exhibited good thermogravimetric stability, with the PFDT/PDA/PI membrane decomposing at a temperature above 138 °C. In between 138 and 210 °C, the weight loss of PFDT/PDA/ PI membrane was 15.5% owing to the decomposition of the organic group (Fig. S3). More significantly, the structure of the PI nanofibrous membrane was preserved even after the modification with PFDT/PDA, but the microstructural surface became altered after the PDA coating (Figs. S4 and S5). Furthermore, Fig. S6 shows an X-ray diffraction (XRD) patterns of the pristine and the corresponding modified PI nanofibrous membranes, in which no significant difference was observed except a decrease in all the peak intensities. This indicated that the membrane was successfully modified by PDA and PFDT/PDA as well as the sustenance of the fiber pattern during the surface treatments.



Fig. 1. SEM images for (a) the pristine PI nanofibrous membranes with an average diameter of approximately 300 nm; (b) PI fibrous membranes treated with PDA solution; (c) the PI nanofibrous membranes treated with PFDT/PDA solution with the surface roughness and fibers diameter being enhanced; and (d) PFDT/PDA/PI membrane after the separation of oil-water mixture.



Fig. 2. (a) FT-IR and (b) XPS spectra of pristine, PDA and PFDT/PDA coated PI fibrous membranes.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2018.06.067.

3.2. Wettability of the PFDT/PDA/PI fibrous membrane

The hydrophobicity as a function of the ammonia content of the as-prepared membranes was characterized. As shown in Fig. 3 for the modified PI nanofibers, t0.4 mL ammonia content revealed some superhydrophobic features. However, at ammonia concentration higher than 0.8 mL, there was a slight decrease in WCAs. This may be due to the surface wettability of nanofibrous membranes being influenced by both the surface roughness and the surface free energy, simultaneously. Furthermore, a high ammonia concentration may lead to the formation of indistinct hierarchical structures (see Figs. S4f and S5f). The hierarchical nanostructure of as-prepared membranes can be tuned precisely by simply controlling the ammonia content.

Furthermore, the surface wettability of the resulting PFDT/PDA/ PI nanofibrous membranes was investigated using contact angle



Fig. 3. Water contact angle measurements from PFDT/PDA/PI fibrous membrane prepared with different amount of ammonia. The corresponding water contact angles were $137.52 \pm 1.15^{\circ}$, $151.23 \pm 0.85^{\circ}$, $152.52 \pm 1.12^{\circ}$, $151.61 \pm 0.96^{\circ}$, $150.75 \pm 1.37^{\circ}$ and $143.46 \pm 1.10^{\circ}$, respectively.

measurements. The PFDT/PDA/PI membranes prepared with 0.4 mL of ammonia was chosen for further study. Fig. 4a shows a sequence of snapshots recorded of a water droplet (2 µL) staying on the as-prepared membrane for 30 min. It was observed that the WCAs was at approximately 153°, indicating superhydrophobic properties, while the superhydrophobic state of PFDT/PDA/PI membranes remained stable for a very long time (see Fig. S7), in contrast to the pristine PI nanofibrous membrane which exhibited some hydrophilicity and oleophilicity features (Fig. S8). The fundamental mechanism of the increased hydrophobicity of PFDT/PDA/ PI nanofibrous membrane surface is depended on the combination of a hierarchical micro-/nano-sized structure and low surface energy [32,33]. The long F-alkyl chains likely resulted into the low interfacial tension of these PI-based membranes [34,35], while the presence of the PDA particles on the surface accounted for the hierarchical surface roughness. Moreover, a straightforward experiment was carried out to understand and predict the wetting behavior of the treated PI nanofibrous membrane (see Fig. S9). Specifically, without 1H, 1H, 2H, 2H-perfluorodecanethiol modification, the PDA/PI nanofibrous membrane cannot achieve the superhydrophobicity (see Fig. S9a). This observation clearly indicated that to make a surface superhydrophobic, it is necessary to create low surface energy surface. Furthermore, as regards to the WCA, the PFDT/PDA treated glass slide was 92° (Fig. S9b), revealing that the superhydrophobicity significantly depended on the microscale nanofiber pattern. Additionally, the surface morphology of PFDT/PDA/PI in Fig. 1c displayed three-dimensional (3D) hierarchical microscales and nanoscales structure roughness, which consists of irregular gaps between nanofibers, while agglomerated PDA particles were uniformly distributed on the PI nanofibers. Hexadecane $(2 \ \mu L)$ (Fig. 4b) and 1,2-dichloroethane (DCE) droplet $(2 \ \mu L)$ (Fig. 4c) were used evaluate the wettability of the asprepared membranes in air and underwater, with the results indicating that the modified membranes were superoleophilic. Moreover, DCE and *n*-hexane were developed to model heavy-(denser than water) and light oil (lower density than water), respectively and the results, as shown in Fig. 4d and e, revealed that the DCE and *n*-hexane droplets $(2 \mu L)$ were readily spread and absorbed by the as-prepared composite membrane within 10 s. Furthermore, the PFDT/PDA/PI nanofibrous membrane exhibited excellent underwater oleophilic properties to a selection of oils, including sunflower oil, olive oil, petroleum ether and flax



Fig. 4. Wettability of the PFDT/PDA/PI membrane. (a) Photographs of a water droplet (2 µL) on the PFDT/PDA/PI membrane showing contact angle of 152°; (b) Photographs of an oil droplet (2 µL, *n*-hexane) on the surface of PFDT/PDA/PI membrane showing nearly zero contact angle in air; (c) Photographs of a DCE droplet (dyed with oil red) in water could be adsorbed by a piece of PFDT/PDA/PI membrane; (d) Photographs of an oil droplet (2 µL, 1,2-dichloroethane (DCE)) on the surface of PFDT/PDA/PI membrane in water; (e) Photographs of an oil droplet (2 µL, *n*-hexane) on the surface of PFDT/PDA/PI membrane in water;

seed oil, with oil contact angles smaller than 10° (Fig. S11). Experimentally, the dynamic hydrophobic performance of the membrane was also determined by measuring advancing/receding (A/ R) and sliding angle. As shown in Fig. 5, after being coated with PDA and low-surface-energy PFDT, the advancing and receding contact angle of the PFDT/PDA/PI membranes are $\approx 155.1^{\circ}$ and \approx 150.7°, while the PFDT/PDA/PI membranes exhibited slight contact angle hysteresis ($\approx 4.4^{\circ}$) and low adhesion. It could be explained that after PDA and low-surface-energy PFDT coating, PI nanofibrous membrane exhibited high water contact angle, thereby more repellence formed by air pockets. Due to the air pockets formed between micro-/nano-structures of the water droplet and the PI nanofibrous membrane, the water droplets cannot be cannot be pumped. Moreover, the adhesive behavior of the water on the as-prepared PFDT/PDA/PI membranes surface was assessed by sliding-angle, in which a sliding angle of $\approx 6.5^{\circ}$ was obtained, confirming that the PFDT/PDA/PI membranes exhibited remarkable superhydrophobicity.

3.3. Theoretical analysis of the solid-water-oil interface

If a water droplet comes in contact with a flat solid surface in air, the water-air and solid-air interfaces come together with a static contact angle, θ_W . The value of θ_W can be given by the Young's equation [36],



Fig. 5. Left: Schematic illustration of the sliding, advancing and receding angle of a liquid droplet. Right: A water droplet sliding at low angle of 6.5°. Corresponding advancing and receding contact angles on the PFDT/PDA/PI membranes were measured to be about 155.1° and 150.7°. Droplet sizes: 8 µL.

where γ_{WA} , γ_{SW} and γ_{SA} are the surface tensions of the water-air, solid-water and solid-air, respectively. A contact angle θ_0 of an oil droplet on a flat solid surface can be expressed by the following equation.

$$\cos\theta_0 = \frac{(\gamma_{SA} - \gamma_{SO})}{\gamma_{OA}} \tag{2}$$

where γ_{SA} , γ_{SO} , and γ_{OA} are the surface tensions of solid-air, solid-oil and oil-air interface, respectively. As indicated in eq. (2), if γ_{SA} is higher than γ_{SO} , then, an oleophilic surface can be obtained.

To create an oleophilic surface, the solid-water-oil interface was studied. If an oil droplet comes in contact with a flat, solid surface, the contact angle characteristic of an oil droplet in water, θ_{OW} [37] is given as:

$$\cos\theta_{OW} = \frac{(\gamma_{SW} - \gamma_{SO})}{\gamma_{OW}} \tag{3}$$

where γ_{OW} , γ_{SW} and γ_{SO} are surface tensions of the oil-water, solidwater and solid-oil interfaces, respectively. According to the equations above, the contact angle, θ_{OW} , can be expressed as follows [38].

$$\cos\theta_{ow} = \frac{\gamma_{OA}\cos\theta_{O} - \gamma_{WA}\cos\theta_{W}}{\gamma_{OW}} \tag{4}$$

Eq. (4) predicts that hydrophilic surfaces ($\theta_W < 90^\circ$, $\gamma_{SA} > \gamma_{SW}$) are usually underwater oleophilic, whereas hydrophobic (θ_W > 90°, $\gamma_{SA} < \gamma_{SW}$) and oleophilic ($\theta_O < 90^\circ$, $\gamma_{SA} > \gamma_{SO}$) surfaces often exhibit oleophilic underwater because of the surface tensions of oil (organic liquids) which are much lower than that of water. The results predicted that the theoretical analyses are in accordance with the experimental results in which the interfacial tension for DCE and water are 23 and 72 mN m⁻¹, respectively, and that the PFDT/PDA/PI membranes were superhydrophobic and superoleophilicity. The superhydrophobicity underwater and micro/nanostructures of the PFDT/PDA/PI formed a wettability characteristic of a three-phase solid-oil-water system. When the PFDT/PDA/PI membranes were immersed in water, the valley of the micro/nanoscale hierarchical structure is filled by oil. When a small water droplet is further dripped onto the membrane surface, the contact area between the water droplet and the PFDT/PDA/PI membrane was decreased significantly.

Considering that surface hydrophobicity is enhanced by surface roughness, the contact angle of the liquid droplet contact with a rough solid surface without air pockets is defined with following equation [39]:

$$\cos\theta = R_f \cos\theta_f \tag{5}$$

where θ_f is the contact angle of a liquid on a rough solid surface (θ_W , θ_O , or θ_{OW}), and R_f is a surface roughness factor, which is given by equation:

$$R_f = \frac{A_{SL}}{A_F} \tag{6}$$

where A_F and A_{SL} are the geometric projected area and actual area of a rough surface, respectively. It is believed that for rough PFDT/PDA/PI nanofibrous membrane, a state between Cassie's and Wenzel's appears, where the droplet penetrates the pores while leaving air pockets below. A solid-water-air composite state is then formed when air is trapped under the droplets in the surface cavities, as shown in Fig. S11. The apparent contact angle (θ_C) could be expressed by the Cassie-Baxter [40] equation:

$$\cos\theta_{\rm C} = R_f f_{\rm SI} \cos\theta_f + f_{\rm SI} - 1 \tag{7}$$

where f_{SL} is an area fraction of the solid-liquid interface. Obviously, the optimization of the chemical compositions (θ_f) and the geometric structures (R_f) are two vital parameters that affect the surface wettability of PFDT/PDA/PI nanofibrous membranes, in which the R_f can be increased significantly by creating hierarchical micro/nanostructures, while hydrophobicity can also be improved further by a low-surface-energy PFDT coating. The AFM analysis in Fig. 6 showed that the root-mean-square (RMS) roughness of PDA and PFDT/PDA coating was 157 and 57.8 nm, respectively. Therefore, the treated membranes were expected to exhibit the remarkable superhydrophobic behavior. Moreover, the WCA increases with decreasing f_{SL} due to a larger surface roughness. Since, the PFDT/PDA/PI nanofibrous membrane has a very rough surface, indicating a smaller f_{SL} , thus a large water contact angle was obtained.

To further describe the separation mechanism of oil and water for the PFDT/PDA/PI membrane, the concept of the intrusion pressure Δp was used to model the water and oil wetting processes [41,42].

$$\Delta p = \frac{2\gamma}{R} = -\frac{l\lambda(\cos\theta_A)}{A} \tag{8}$$

Here γ is the interfacial tension of liquid, ι is the circumference of the membrane pore, A is the cross-sectional area of the membrane pore and θ_A represents the water contact angle on the modified membrane. From Equation (8), the modified membrane is oleophilic with $\theta_A < 90^\circ$ and $\Delta p < 0$, indicating that the oil can permeate the membrane because in such cases the membrane cannot support any pressure. Meanwhile, when the surface is superhydrophobic and $\theta_A > 90^\circ$, then $\Delta p > 0$, which in this case, to some extent, the PFDT/PDA/PI membrane can withstand the pressure and water cannot permeate through the modified membrane, Ss shown in Fig. 7. This work demonstrates the as-prepared membrane exhibited both superhydrophobicity and superoleophilicity, with $\theta_A > 90^\circ$, which indicates that $\Delta p > 0$, therefore, oil can permeate through the membrane spontaneously. Furthermore, oil is trapped between the PFDT/PDA and PI nanofiber during the separation process. The trapped oil is nonpolar which then repels the polar water. This resulted into an increase of the repulsive force between the water and modified membrane. Therefore, membrane prewetted with oil was used for separation of oils heavier than water. Because the oily environment was formed on the surface of prewetted membrane, it repels the water completely, preventing them from passing through the membrane, hence, water cannot permeate the membrane when $\theta_A > 90^\circ$ and $\Delta p > 0$. Based on the above discussion, the modified membrane exhibits excellent superhydrophobicity and superoleophilicity.

3.4. Oil-water separation performance

Various kind of oil-water mixtures including DCM-water, dichloromethane-water, carbon tetrachloride-water, bromobenzene-water and trichloromethane-water have been separated by an in-house built separation setup (Fig. 8), During the entire separation process, the maximum flux obtained using the PFDT/PDA/PI nanofibrous membrane was $8100 \pm 100 \text{ Lm}^{-2} \text{ h}^{-1}$



Fig. 6. AFM images of (a) PDA and (b) PFDT/PDA coatings on glass slide. The root-mean-square (RMS) roughness was 157 and 57.8 nm, respectively.



Fig. 7. Schematic diagrams of the liquid wetting model on the as-prepared PFDT/PDA/PI nanofibrous membrane. (a) In air, the membrane shows superhydrophobicity that can sustain the water and can also be permeable to oil, because $\Delta p > 0$. (b) In air, the membrane displays superoleophilicity that oil can permeate through the membrane, as it cannot support any pressure because $\Delta p < 0$. (c) After the oil permeation, some oil can be trapped among the interstices between the PI nanofibers and SNPs, thus the membrane shows superhydrophobicity, and water can be supported by the membrane, because $\Delta p > 0$. O is the center of the spherical of the meniscus; O₁ and O₂ are the cross-section center of the membrane. R is the curvature radius of the spherical of the meniscus.



Fig. 8. Separation images for immiscible oil/water mixtures.

for a DCM-water mixture. In addition, the membrane showed high separation efficiency for different types of oil-water mixtures (above 99%) (Fig. 9). This result implied that the PFDT/PDA/PI membranes are promising candidates in treating a large amount of oil/water mixtures. Fig. 10 shows the separations performance of the PFDT/PDA/PI nanofibrous membrane as function of membrane thickness. As can be clearly seen, the permeate flux decreased significantly with increasing membrane thickness, with the separation efficiency remaining above 99%. The decrease in the flux was ascribed to the lower porosities of the thicker membrane (Fig. 10c), while the high flux and separation efficiency of the modified membrane was due to its pore size and pore size distribution, with the N₂ adsorption-desorption results (Fig. S13) clearly demonstrating this.

Beside the surfactant-free oil-water mixture, surfactantstabilized water-in-toluene was prepared and studied (Fig. 11). The filtration device employed was the same as that for the separation of free oil-water mixture (Fig. 8), with the membrane being fixed at the middle of the device and the emulsion poured onto the membranes. Due to the underwater superoleophilicity of the membrane and that the toluene-prewetted membrane was in contact with the water-in-toluene emulsions, toluene could permeate freely through the membrane with gravity acting as the driving force only, whereas the water was repelled on the superhydrophobic surface and the milky emulsion became transparent after the separation (Fig. 11b). The pristine PI and PDA/PI nanofibrous membranes were also used for comparison. For pristine PI nanofibrous membranes, the filtrate solution maintained the semitransparency after separation, while the filtrate solution turned transparent after separating with PDA/PI nanofibrous membrane, suggesting that the untreated PI nanofibrous membrane cannot separate stabilized emulsion (Fig. S14c). Optical microscopy pictures of the emulsions before and after separation were also observed. As shown in Fig. 11a, the feed emulsions



Fig. 9. Flux (a) and Separation efficiency (b) of various oil-water mixtures through PFDT/PDA/PI nanofibrous membrane.



Fig. 10. (a) Flux of DCE through PFDT/PDA/PI nanofibrous membranes with different thickness. (b) Separation efficiency of these membranes for DCE-water mixtures. (c) Porosity of PFDT/PDA/PI nanofibrous membranes with different thickness.



Fig. 11. (a, c) The optical microscope images of the water-in-toluene emulsion before and after separation; (b) The digital images of the water-in-toluene emulsion before and after separation; (d, e) Particle size analysis of the water-in-toluene emulsion before and after separation.

contain numerous water droplets, while no droplets were observed (Fig. 11c) in the collected filtrates, which further proven the effectiveness of the PFDT/PDA/PI membranes for separating water-intoluene emulsions. Significantly, a series of other surfactantstabilized water-in-oil emulsions including water-in-hexane, water-in-kerosene and water-in-chloroform were successfully separated by the as-prepared membrane. In addition, the prepared surfactant-stabilized water-in-oil emulsions exhibited excellent stability (Fig. S14). The optical microscope photographs of the demulsification and separation results for other kinds of emulsions were also obtained (Fig. S15). Moreover, the droplet size of the water-in-toluene emulsions before and after separation was shown in Fig. 11d-e, with the sizes of the uniformly water droplets dispersed in the toluene ranging from 100 nm to 400 nm before separation. However, a reduction in size of less than 10 nm in the filtrate was collected after separation, indicating that the pore size in the membrane is far smaller than the minimum droplet size of the emulsion. In addition, the droplet sizes of other water-in-oil

emulsions before and after separation were also determined as presented in Fig. S16. All the tested emulsions possess droplet sizes of less than 1000 nm in the feed solution (Fig. S16a–d) while the droplet size of collected filtrate for different emulsion systems was around 10 nm (Fig. S16e–h), which confirmed that the PFDT/ PDA/PI membrane showed excellent separation ability. Notably, SEM images (Fig. S17) after the separation revealed that there was no visible change to the morphology and structure of PFDT/ PDA/PI nanofibrous membrane. From the discussed above, the versatility of the designed nanofibrous membranes is proven.

3.5. Recyclability and stability of PFDT/PDA/PI fibrous membrane

tTe recyclability and stability, as important criterions for practical oil-water separation applications of the obtained membrane, were also investigated. Fig. 12 depicts the separation ability of the PFDT/PDA/PI nanofibrous membrane after 20 consecutive cycles for DCM-water mixture, which clearly shows the flux with



Fig. 12. Change in Flux (a) and (b) of DCE through electrospun PFDT/PDA/PI nanofibrous membrane with 20 times number of cycle. (c) Oil concentration in the collected water after separating various kinds of oil-water mixtures for twenty times cycles.



Fig. 13. WCA of the PFDT/PDA/PI nanofibrous membranes. (a) As a function of the pH of the water in the oil-water mixtures; (b) when heated in air at different temperatures and (c) after calcination in air at different temperatures for 10 min.



Fig. 14. Mechanical strength and abrasion resistance of PFDT/PDA/PI nanofibrous membranes. (a) Stress-strain curves of PI nanofibrous membrane. (b) Schematic illustration of a sandpaper abrasion test. (c) Process of the sandpaper abrasion cycle. d) WCA after every abrasion test. The data presented were obtained by measuring five different positions, while the average was taken.

a very small variation (Fig. 12a), while the separation efficiency was still above 98% (Fig. 12b) and the ultralow oil content below 5 ppm (Fig. 12c), indicating the high stability and reusability of the membranes.

Moreover, the stability of the superhydrophobicity and superoleophilicity PFDT/PDA/PI nanofibrous membrane was investigated at two different high-temperatures. The selected superhydrophobicity and superoleophilicity membrane was calcined at temperatures of about 120 °C and about 250 °C for 60 min, in air respectively. After being heat-treated, the correlation between temperature and WCA was presented (Fig. 13). The results clearly showed the high thermal stability property of the superhydrophobicity and superoleophilicity PFDT/PDA/PI nanofibrous membrane. In addition, the chemical stability test was carried out to evaluate the wettability of PFDT/PDA/PI membrane as a function of pHs. As shown in Fig. 13a, the WCAs of the modified membrane were still maintained at about 150°, indicating that the as-prepared membranes possess excellent acid and alkali corrosion resistance, while still sustaining their superhydrophobicity with very small variation after being exposed to air over 100 days at room temperature (Fig. S18).

Robustness is another important limitation to practical application of oil-water separation. In our current study, both the stressstrain curves and sandpaper abrasion were investigated to test the mechanical stability of the PFDT/PDA/PI fibrous membrane. Fig. 14a showed the stress-strain curves of the PI membrane. The tensile stress at break of the nanofiber membranes can reach 450 MPa, a value high enough to enable the membrane suitable for separating the oil-water mixture without any substrate. A schematic of the sandpaper abrasion experiment was done to test the durability. As shown in Fig. 14b, a performance of 5 cycles of 15 cm abrasive length with a 50 g weight as an external force was depicted. Furthermore, the WCA data (Fig. 14d) and SEM (Fig. S20) collected after the abrasion 5 cycles tests revealed that the PFDT/PDA/PI fibrous membrane did not lose their superhydrophobicity.

4. Conclusions

In conclusion, highly flexible, self-supporting and superhydrophobic PFDT/PDA/PI membranes were prepared via the introduction of PFDT/PDA functional layer to the electrospun PI nanofibrous membrane. The resultant, as-prepared PFDT/PDA/PI membrane could be used for oil-water separation with high flux of $8018.5 \pm 100 \text{ Lm}^{-2} \text{ h}^{-1}$ and separation efficiencies of above 99%, in addition to having remarkable cyclability of at least 20 cycles of repeated oil-water separation with constant superhydrophobicity and fixed separation efficiency, while also possessing excellent environmental durability under extreme conditions (mechanical abrasion, harsh environment and various chemical solvents). The reported approach presented in this study is versatile, economic and can be performed in an environmentally-benign way, which can be readily extended to fabricate other novel membrane materials with stable superhydrophobicity for various applications.

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