Dual pH- and ammonia-vapor-responsive electrospun nanofibrous membranes for oil-water separations

Wenjing Maa,d,1, Sangram Keshari Samalb,1, Zhongche Liu, Ranhua Xiongb, Stefaan C. De Smedtb, Bharat Bhushand, Qilu Zhangc, Chaobo Huangb,e

a College of Chemical Engineering, Jiangsu Key Lab of Biomass-Based Green Fuels and Chemicals, Nanjing Forestry University (NFU), Nanjing 210037, PR China
b School of Material Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, PR China
c Lab General Biochemistry & Physical Pharmacy, Department of Pharmaceutics, Ghent University, 259000, Belgium
d Nanoprobe Laboratory for Bio- & Nanotechnology and Biomimetics (NLBB), The Ohio State University, Columbus 43210-1142, USA

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ABSTRACT

In the last few years, the amount of industrial oily wastewater discharge and number of oil spill accidents have increased exponentially [1–3], spurring the development of highly efficient, cost-effective oil-water separation technologies. In this study, a dual pH- and ammonia-vapor-responsive polyimide (PI)-based nanofibrous membrane with high permeate flux and stability was developed for oil-water separations. The membrane was prepared by successively dip-coating electrospun PI in decanoic acid (DA)-TiO2 and silica nanoparticles (SNPs). The novel SNP/DA-TiO2/PI membrane exhibits superhydrophobicity in air and superoleophilicity in neutral aqueous environments (e.g., at pH 6.5). However, the membrane becomes hydrophilic and superoleophobic in basic aqueous environments (e.g., at pH 12), resulting in only water permeation during oil-water separations. The oil-water separation potential of this innovative dual-responsive membrane was investigated using several model oil-water mixtures. The membrane has extremely high flux (6500 ± 100 L m−2 h−1) and separation efficiency (> 99%) and is reusable. In addition, thermal stability and abrasion resistance tests show that the membrane is highly stable under extreme conditions. This dual-responsive electrospun nanofibrous membrane has potential for use in industrial oil-polluted water and oil spill treatment and in systems that require selective oil-water permeation. Furthermore, changes in the surface wettability can also be induced by exposure to ammonia vapor, which might facilitate remote-controlled oil-water separations.

1. Introduction

Recently, the amount of industrial oily wastewater discharge and number of oil spill accidents have increased exponentially [1–3], spurring the development of efficient, cost-effective oil-water separation technologies [4], such as gravity processing [5], skimming [6], air flotation [7], sedimentation under centrifugal fields [8], electrocoalescence [9], and biological treatments [10]. Although these technologies have some advantages, most of them also suffer from drawbacks such as a low separation efficiency or a high energy consumption [11,12]. In the last few years, some membrane-based technologies with excellent oil-water separation potential have been developed.

The surface wettability of the separation membrane is a key factor affecting its oil-water separation performance [13]. Hence, membranes with tailored wettability have been developed for effective oil-water separation [14]. Inspired by the unique surface properties of lotus leaves, silver ragwort leaves and water strider legs, researchers have found that multiple nanometer- and/or micron-sized surface features can remarkably enhance the material wettability, resulting in superhydrophobic or superoleophobic properties [15,16]. In a recent study, Xue et al. reported the preparation of a novel micro-/nano-hierarchically structured polyacrylamide (PAM) hydrogel-coated mesh [17]. They showed that this film could be easily wetted by water but exhibited anti-wetting properties against oils due to its superhydrophobicity and underwater superoleophobicity. Hence, only water permeated the film, resulting in selective oil-water separation [18]. However, the PAM-coated mesh exhibited poor environmental adaptability; it easily swelled when hydrated and softened. In a later study, Zhang et al. prepared a novel inorganic Cu(OH)2 nanowire-haired copper mesh with superhydrophobicity and underwater ultralow adhesive superoleophobicity. The resulting membrane material effectively separated both immiscible oil-water mixtures and oil-in-water emulsions by a gravity-
driven process with extremely high separation efficiencies and separation capacities [19]. Membranes have also been prepared from other materials, such as multifunctional polyurethane foams [20], carbon nanotube hybrid films [21] and carbon-silica nanofibrous membranes [22], for oil-water separations.

Stimulus-responsive polymeric membranes respond to changes in the surrounding environment, i.e., to various external stimuli, such as temperature changes [23], pH changes [24], light irradiation [25], ionic strength changes [26], electric fields [27] and magnetic fields [28]. The ability of stimuli-responsive membranes to reversibly change their surface wettability when exposed to an external stimulus has made them attractive for use in a wide range of applications, including enzyme immobilization [29], sensors [30], reversible cell capture [31], controlled drug delivery [24,32], catalysis [33], and liquid mixture (oil-water) separation [34]. Previously, Cheng et al. [35] fabricated a novel pH-responsive copper mesh membrane for oil-water separations by assembling responsive thiol-functionalized molecules on a Cu(OH)₂ nanorod substrate. The film underwent a superhydrophobic-to-superhydrophilic transition when the environment was changed from acidic to basic.

Electrospinning is a versatile technique that has been shown to be suitable for preparing nano- or submicron-sized fibers [36,37]. Electrospun nanofibrous membranes exhibit several unique and interesting properties, such as a high surface area-to-volume ratio, a high void volume fraction, tunable surface functionalities, interconnected open structure and high stability, which lead to high-quality effluents. Therefore, these membranes are suitable for oil-water separations [38]. Che et al. [39] recently fabricated a CO₂-responsive oil-water separation membrane by electrospinning poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) onto a substrate to obtain a nanostructured surface morphology. The oil-water wettability of the resulting membrane could be adjusted by switching between CO₂ and N₂ stimuli; therefore, these membranes are promising for CO₂-controlled oil/water on-off switching. Despite the promising results obtained with electrospun nanofibrous membranes, much work in developing new membranes for separation technologies remains to be done.

In this study, a novel dual pH- and ammonia-vapor-responsive membrane was fabricated by solution dip-coating an electrospun polyimide (PI) nanofibrous membrane. PI-based nanofibrous membranes are considered to be one of the most versatile membrane types due to their excellent mechanical strength, flexibility, stability, etc. [40–42] and have therefore been widely used in various high-tech fields [43,44]. In this study, the dual-responsive PI membrane was prepared by dip-coating the electrospun PI nanofibrous membranes in a decaenoic acid (DA)-TiO₂ mixture and a silica nanoparticle pre-gel solution, followed by high-temperature annealing (Scheme 1). The membrane surface morphology and composition were characterized by field emission scanning electron microscopy (FE-SEM) and Fourier transform infrared (FT-IR) spectroscopy. Contact angle measurements were performed to characterize the surface wettability under neutral and basic conditions. The pH- and ammonia-induced wettability transitions and selective oil-water permeation of the prepared membranes are discussed in detail. A theoretical analysis of the solid–water–oil interface was also performed to further understand the pH-induced wettability transition. Furthermore, the oil-water separation performance of the PI nanofibrous membrane was evaluated using different oil-water mixtures.

2. Experiment

2.1. Materials

All chemicals and solvents were used as received, unless otherwise stated. Tetraethyl orthosilicate (TEOS), tetraethyl orthotitanate (Ti (OBu)₄), decaenoic acid (DA), methylene blue, oil red, silica (SiO₂) sol (50 nm) and hexadecyltrimethylammonium bromide were provided by Shanghai Aladdin Industrial Corporation. N,N-Dimethylacetamide (DMAC), dichloromethane (DCM), acetone, trichloromethane, anhydrous ethanol, n-hexane and petroleum ether were purchased from Nanjing Chemical Reagent Co., Ltd. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) (Changzhou Sunlight Pharmaceutical Co., Ltd.) and p-phenylenediamine (PDA) (Shanghai Aladdin Industrial Corporation) were sublimated under reduced pressure before use.

2.2. Instrumentation and characterization

PI nanofibrous membranes were fabricated using an FM1206 electrospinning device (Beijing Future Material Sci-tech, China). Proton nuclear magnetic resonance (¹H NMR) spectra were recorded using an Avance III HD 600 MHz spectrometer (Bruker BioSpin). The membrane structural properties were characterized by FT-IR. Specifically, the absorbance spectra were recorded using a Nicolet 360 FT-IR spectrometer with 32 scans at a resolution of 4 cm⁻¹ over the range of 400–4000 cm⁻¹. The membrane morphology was characterized using a transmission electron microscope (TEM) (JEM-1400, JEOL, Japan) and field emissions scanning electron microscope FE-SEM (S-4800, Hitachi, Ltd., Japan). The FE-SEM was equipped with an Energy Dispersive Spectrometer (EDS). The contact angles of the samples were measured at three different surface spots at 25 °C using a contact angle instrument (JCC2000D1, Shanghai Zhong Chen Digital Technic Apparatus Co., Ltd.,), and the measurements for each sample were averaged. The mechanical properties of the nanofibrous membrane samples were measured at room temperature using an electronic universal testing machine (UTM6502, Shenzhen Sans Technology Stock, China). The polyamide acid (PAA) molecular weight was measured at 35 °C using a gel permeation chromatograph (GPC) (Agilent Technologies, Germany) equipped with one column (PGel 5 μm MIXED-C, Agilent) and a refractive index detector (Bryce). The elution phase was THF (elution rate, 1 mL/min), and a series of polystyrene (PS) standards were used to construct the calibration curve. X-ray photoelectron spectroscopy (XPS) (AXIS Ultra DLD, UK) was employed to analyze the elemental content of the nanofibrous membrane surface. The membrane surface roughness was determined at room temperature using an atomic force microscope (AFM) (Dimension Edge, Bruker, Germany) in tapping mode. The membrane structure was determined by X-ray powder diffraction (XRD) (Ultima IV, Rigaku, Japan). The Barrett–Joyner–Halenda (BJH) pore volume was determined from N₂ adsorption-desorption isotherms recorded at 393 K (Quantachrome, USA), and the pore size distribution (PSD) was obtained from the adsorption branch data. The surface charge of the SNPs/DA-TiO₂/PI membranes were measured on SurPASS solid surface zeta potential analyzer (Anton Paar 3, Austria). KCl solution (1 mmol L⁻¹) was chosen as the electrolytic solution and circulated through the measuring cell. Multiple rinsing and flow check steps were carried out prior to the tests to ensure reproducibility.

2.3. Polyamide acid (PAA) synthesis

PAA was synthesized by the low-temperature polycondensation of 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) with p-phenylenediamine (PDA), as shown in Fig. S1. The PAA synthesis is described in detail in a previous report [11]. Briefly, BPDA (2.9422 g, 0.01 mol) and PDA (1.0814 g, 0.01 mol) were dissolved in 40 mL of DMAC in a three-necked round bottom flask under vigorous mechanical stirring at −5 °C in a nitrogen environment. After 24 h, the reaction was terminated by exposure to air at room temperature. The average molecular weight and dispersity of the obtained polymer were measured by gel permeation chromatography.

2.4. Polymide (PI) nanofibrous membrane fabrication by electrospinning

The electrospinning procedure was performed according to a
previously described protocol [11]. The as-prepared PAA was dissolved in DMAC under vigorous stirring for 5 h to form a 3 wt% precursor solution. Then, 1 wt% hexadecyltrimethylammonium bromide was added to increase the solution conductivity. The PAA solution was electrospun using metal needles with an inner diameter of 0.6 mm. A rotational flywheel with a speed of 1500 rpm was employed to collect the electrospun fibers, which were spun at a speed of 1.5 mL h\(^{-1}\). The distance between the needle tip and collector was 10 cm, and the voltage was 25 kV (+15, −10 kV). The electrospinning setup is shown in Scheme 1. The FT-IR spectrum of the resulting membrane is shown in Fig. S2 in the Supplementary material. The PI nano-fibrous membrane was obtained by imidization of the electrospun PAA nano-fibrous membrane using the following temperature program: 150 °C/1 h, 200 °C/1 h, 250 °C/1 h, 300 °C/1 h, 350 °C/3 h and 380 °C/30 min.

2.5. Preparation of the SNP/DA-TiO\(_2\) coating solution

First, 0.3 g of Ti(OBu)\(_4\) and 0.18 g of decanoic acid were dissolved in 2.5 mL of ethanol and 10 mL of ethanol, respectively, in round-bottom flasks. Then, the two solutions were combined and stirred vigorously for 10 min. Next, 20 \(\mu\)L of a 0.1 M HCl aqueous solution and 150 \(\mu\)L of water were added to the mixture while stirring. The resulting solution was then stirred for another 10 min to obtain a TiO\(_2\) sol, and 3 mL of 1 wt% silica nanoparticles (dispersed in ethanol) was subsequently added to the sol. Finally, the coating solution was vigorously stirred for 60 min. All the procedures were performed at room temperature.

2.6. Preparation of the SNP/DA-TiO\(_2\)/PI nano-fibrous membranes

To modify the PI nano-fibrous membranes with SNP/DA-TiO\(_2\), the electrospun PI membranes were first washed successively with acetone, ethanol and water and then dipped in the SNP/DA-TiO\(_2\) coating solution for 10 min. The dipped membrane was removed from the solution and allowed to dry at room temperature for 1 h and then at 60 °C for 20 min. Finally, the membrane surface was cured under reduced pressure at 120 °C for 30 min.

2.7. Preparation of the oil-water mixtures

The oil-water mixtures were prepared by mixing 10 mL of oil and 10 mL of water in a beaker under ultrasonication. The oil and water phases were dyed with oil red and methyl blue, respectively.

2.8. Evaluation of the membrane separation ability

To assess the permeate flux and separation efficiency of the prepared SNP/DA-TiO\(_2\)/PI nano-fibrous membranes, they were positioned between two glass funnels with an effective separation area of 56.25 \(\times\) 10\(^{-6}\) m\(^2\), and the oil-water mixture was flowed through them.

The liquid flux (F) was calculated using Eq. (1):

\[
F = \frac{V}{A \Delta t}
\]

where V (L) is the filtered liquid volume, A (m\(^2\)) is the effective membrane area in the setup, and \(\Delta t\) (h) is the permeation time.

The separation efficiency (\(\eta\)) was calculated using Eq. (2):

\[
\eta = \frac{V_1}{V_0} \times 100
\]

where \(V_0\) and \(V_1\) are the water volumes before and after the separation process, respectively.

2.9. Evaluation of the nano-fibrous membrane porosity (P)

The electrospun PI nano-fiber membrane porosity was calculated according to literature methods using the following equations [45]:

\[
\rho_{\text{membrane}} = \frac{\text{mass}_{\text{membrane}}}{\text{area}_{\text{membrane}} \times \text{thickness}_{\text{membrane}}}
\]
\[
\frac{\rho_{\text{film}}}{\rho_{\text{membrane}}} = \frac{\text{mass}_{\text{film}}}{\text{area}_{\text{film}} \times \text{thickness}_{\text{film}}} 
\]

(4)

\[
P = \left(1 - \frac{\rho_{\text{membrane}}}{\rho_{\text{film}}}\right) \times 100\%
\]

(5)

where \(\rho_{\text{membrane}}\) and \(\rho_{\text{film}}\) are the densities of the electrospun PI nanofibrous membrane and film, respectively.

3. Results and discussion

3.1. Characterisation of the SNP/DA-TiO\textsubscript{2}/PI nanofibrous membranes

The morphologies of the PI nanofibrous membranes before and after treatment with the SNP/DA-TiO\textsubscript{2} solution were characterized by field emission scanning electron microscopy (FE-SEM). As shown in Fig. 1a, the pristine PI fibers were uniformly distributed with an average diameter of approximately 300 nm. The high-magnification image in the inset in Fig. 1a reveals that the PI nanofibrous membrane surface was quite smooth. As shown in Fig. 1b, the PI nanofibers were uniformly covered with a thin DA-TiO\textsubscript{2} layer after treatment with the DA-TiO\textsubscript{2} sol. Furthermore, silica NPs were also observed on the fiber surfaces after treatment with the SNP/DA-TiO\textsubscript{2} solution (Fig. 1c). The silica NPs embedded in the fiber surface were expected to increase the membrane surface roughness and, hence, the surface hydrophilicity/hydrophobicity.

In addition to the surface roughness and compositional characterizations of the treated PI nanofibrous membranes, the fiber patterns of the membranes were also studied to ascertain the effects of the treatments. As shown in Fig. S3, the X-ray diffraction (XRD) patterns of the modified PI nanofibrous membranes were the same as that of the pristine membrane, except that the intensities were lower, indicating that the fiber pattern was preserved during the surface treatments.

3.2. pH-responsive wettability of the SNP/DA-TiO\textsubscript{2}/PI nanofibrous membranes

The pH-responsive wettability of the SNP/DA-TiO\textsubscript{2}/PI nanofibrous membranes was evaluated by measuring the contact angles (CAs) of water and oil droplets on the surfaces at various pH values. Fig. 3a shows snapshots of a water droplet (2 \(\mu\)L, pH 6.5) on the membrane taken within the first 180 s. The water CAs (WCAs) were found to be approximately 155°, indicating that the surface was superhydrophobic. It should be noted that this superhydrophobicity was quite stable and lasted for a very long time in air (see Figs. 3a and f and S4). In contrast, the unmodified electrospun PI nanofibrous membrane was both hydrophilic and oleophilic (Fig. S5). The enhanced hydrophobicity of the treated PI membrane surface was attributed to its low surface energy and high surface roughness, as discussed in Section 3.1. The low surface energy of these PI-based membranes likely resulted from the long DA C-H asymmetric deformation and aliphatic carbon bonds, carbonyl stretching and the SNP Si–O–Si symmetric stretching vibrations, respectively, indicating that the PI nanofibrous membrane was successfully modified by SNP/DA-TiO\textsubscript{2}. The presence of titanium and silicon in the modified membranes was detected by XPS (Fig. 2b), further confirming their successful modification by DA-TiO\textsubscript{2} and SNP/DA-TiO\textsubscript{2}.

The presence of SNP and DA-TiO\textsubscript{2} on the modified PI nanofibrous membranes was confirmed by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The absorption peaks in the PI fiber FT-IR spectrum (Fig. 2a) at 1716, 1771 and 1356 cm\(^{-1}\) were assigned to the PI –COOH, –CONH and C–N stretching vibrations, respectively, demonstrating the successful electrospinning of the polymer. The absorption peaks in the SNP/DA-TiO\textsubscript{2}/PI nanofibrous membrane spectrum at 1455, 1710 and 792 cm\(^{-1}\) were attributed to the DA
alkyl chains, whereas the nanoscale/microscale surface roughness was due to the presence of the SNPs and possibly the DA residues on the surface. A simple experiment was designed to confirm these effects of the surface modification, and the results are shown in Fig. S6. Specifically, the PI nanofibrous membrane modified by only DA-TiO$_2$ had a WCA of approximately 121° at pH 6.5, indicating that the nanoscale roughness provided by the silica NPs was a key factor leading to the surface superhydrophobicity. Moreover, a glass slide treated with SNP/DA-TiO$_2$ had an even lower WCA of 95° (pH 6.5, Fig. S6b), showing that the microscale nanofiber pattern contributed significantly to the superhydrophobicity.

In addition to the water wettability, the oil wettability of the SNP/DA-TiO$_2$/PI nanofibrous membranes was also investigated. As shown in Fig. 3b, the low oil CA (OCA) of approximately 17.4° measured for an n-hexane droplet (2 μL) within 6 s revealed that the modified membranes were superoleophilic. The underwater superoleophilicity was also evaluated using a 1,2-dichloroethane (DCE) droplet (2 μL) (Fig. 3c). The oil was completely absorbed by the SNP/DA-TiO$_2$/PI nanofibrous membranes within 12 s. Furthermore, n-hexane was used to model light oil (lower density than water). As shown in Fig. 3d, the n-hexane...
droplet (2 μL) spread over a large area and was absorbed by the membrane within only 10 s under water at pH 6.5. The underwater superoleophilicity of the PI-based membrane makes it promising for use in oil absorption from oil-water mixtures (Fig. 3e and f).

In contrast to the superhydrophobic and superoleophilic properties observed at pH 6.5, the SNP/DA-TiO2/PI nanofibrous membrane surfaces exhibited the opposite properties under basic conditions. As shown in Fig. 4a and e, the WCA on the membrane surface decreased rapidly from approximately 150° to almost 0° within 180 s at pH 12. This change in the surface wettability from superhydrophobic to superhydrophilic was attributed to the titanium-carboxylate coordination bond breaking under basic conditions [46–48]. In the preparation of SNPs/DA-TiO2 coating solution, coordination chemistry of DA-TiO2 happened, thus the formation of the ≡Ti–O–Ti–OOC–. However, after being immersed in pH 12 water and ammonia exposure, the ionic DA disappearing and form ammonium carboxylate ions (–COO−NH4+), respectively. FT-IR and Zeta potentials of the prepared membrane were also measured to explain for this (Fig. S7). One consequence of this bond cleavage was the migration of the ionized DA from the solid–air interface to the water–air interface and even into the water phase due to the attractive forces between the ionized DA and the water molecules. The desorption of the low-free-energy DA molecules from the solid surface might have led to an increase in the free energy of the membrane surface and thus to a hydrophilic surface. Moreover, the ionic DA molecules, which can be considered to be surfactants, could reduce the water surface tension by migrating to the water–air interface or water phase. Therefore, the change in the surface wettability resulted from both an increase in the free energy of the solid surface and a decrease in the water surface tension [46]. The migration of the DA molecules from the solid surface to the water was confirmed by 1H NMR experiments with deuterium oxide (D2O, pD 7), in which an SNP/DA-TiO2/PI nanofibrous membrane sample was wetted with D2O and then immersed in water at pH 12 (Fig. S8). In fact, the hydrophobic-to-hydrophilic transition was irreversible, indicating that the DA molecules must be adsorbed on the SNP/DA-TiO2/PI nanofibrous membrane surface for it to exhibit superhydrophobicity. Furthermore, the pH dependence of the WCAs over the pH range of 8–13 reveals that the membrane surface wettability depended on the pH (Fig. S9).

Next, the underwater oil wettability of the membranes was investigated at pH 12. Both heavy and light oils formed stable, nearly spherical droplets on the as-prepared SNP/DA-TiO2/PI nanofibrous membrane, indicating that the membrane surface was highly oleophilic (Fig. 4b–e). For example, DCE (heavy oil) droplets had an OCA of approximately 161.5° on the membrane surface at pH 12 (Fig. 4b), and the underwater superoleophobicity lasted for up to 30 min (Fig. 4e). In fact, even after immersion in water at pH 12 for 7 days, the SNP/DA-TiO2/PI membrane still retained its underwater superoleophobicity (Fig. S10). In addition to DCE, the underwater OCAs of light oils such as olive oil, n-hexane, sunflower oil, and petroleum ether were high at pH 12 (Fig. 4d).

As previously described, the surface wettability of the SNP/DA-TiO2/PI nanofibrous membrane could be changed from superhydrophobic/superoleophilic to superhydrophilic/superoleophobic by varying the pH, indicating that the membrane exhibited pH-responsive surface properties. Due to the tunability of the membrane surface wettability, this membrane could be utilized to perform oil-water separations under various conditions. As shown in Fig. 3f, oil-water mixtures could be separated by the SNP/DA-TiO2/PI nanofibrous
membrane in an in-house built setup; only oil permeated the membrane at pH 6.5. In contrast, at pH 12, the oil phase could not permeate the membrane, whereas water easily passed through the membrane due to the surface wettability transition (Fig. 4f).

3.3. Ammonia-vapor-responsive wettability of the SNP/DA-TiO$_2$/PI nanofibrous membrane

The surface wettability transition could also be induced by exposure to ammonia vapor, which might expand the application of this smart material. As shown in Fig. 5a, nearly spherical neutral water droplets on the SNP/DA-TiO$_2$/PI nanofibrous membrane spread out after exposure to ammonia vapor. This result shows that ammonia vapor could also effectively induce the superhydrophobic-to-superhydrophilic transition of the membrane surface.

A proof-of-concept oil-water separation study was performed using ammonia vapor as the trigger for the SNP/DA-TiO$_2$/PI nanofibrous membrane surface wettability transition. As shown in Fig. 5b, the as-prepared membrane was placed between two flanged glass tubes. A beaker was placed under the tubes to receive the filtered water. To perform the oil-water separation, the upper tube was filled with a small amount of distilled water to form a thin water layer on the superoleophilic nanofibrous membrane. An oil (n-hexane dyed with oil red)-distilled water (dyed with methylene blue) mixture was subsequently poured into and retained in the upper glass tube due to the superhydrophobicity of the membrane. Ammonia vapor was then introduced into the lower tube through a long injection needle. After exposure to the ammonia vapor, the membrane became wettable by water, enabling the water to selectively pass through it (Fig. 5b). Meanwhile, the oil in the mixture was repelled by the superoleophobic membrane and was therefore retained in the upper glass tube. No external forces, except gravity, were applied during the separation procedure. More importantly, these results show that oil-water separations could be remotely controlled by the ammo-

Fig. 5. (a) Photographs water droplets on SNPs/DA-TiO$_2$/PI nanofibrous membrane before and after exposed to ammonia vapor demonstrating the ammonia vapor responsive wettability of the membrane surface; and (b) separation of water from oil-water mixture by the SNPs/DA-TiO$_2$/PI nanofibrous membrane induced by ammonia vapor. Water and oil are dyed with methylene blue and oil red, respectively, to help the observation.

Fig. 6. AFM images of (a) DA-TiO$_2$ and (b) silica NPs/DA-TiO$_2$ coatings on glass slide. The root-mean-square (RMS) roughness was 0.358 and 12.6 nm, respectively.
nia-vapor-responsive wettability of the membrane, which could be useful in dangerous environments.

3.4. Theoretical investigation of the solid–water–oil interface

The pH-induced wettability transition of the solid–water–oil interface is theoretically analyzed in this section to provide further insight into this process. The superhydrophobicity and high WCAs of the fabricated SNP/DA-TiO$_2$/PI membrane can be described by the following equation [49]:

$$\cos \theta = f_1 \cos \theta - f_2$$

(6)

where $\theta$, and $\theta$ are the water contact angles on the rough and smooth membrane surfaces, respectively. For the membrane surface in this study, $\theta$ and $\theta$ were $155^\circ$ (Fig. 3a) and $95^\circ$ (Fig. S6), respectively. The variables $f_1$ and $f_2$ are the solid and air fractions, respectively, under the water droplet; hence, $f_1 + f_2 = 1$. Solving Eq. (6) gives an $f_2$ value of 0.128. Under basic conditions, the titanium-carboxylate coordination bonds were cleaved, resulting in the loss of DA molecules from the surface and thus an increase in the hydrophilicity of the membrane surface (Fig. 4a). According to the Wenzel equation [50], the surface hydrophilicity was enhanced by the high surface roughness, resulting in a superhydrophilic surface. The nanostructural features of the SNP/DA-TiO$_2$/PI membrane surface were preserved after DA desorption, as shown by the AFM analysis (Fig. 6). This result reveals that the surface roughness was mainly due to the silica NPs. In fact, at pH 12, water could enter the PI nanostructures due to capillary forces.

As previously stated, the underwater superoleophobicity of the membrane at pH 12 was attributed to an increase in the free energy of the solid surface and a decrease in the water surface tension. A solid-water-oil interface formed when an oil droplet was placed on the membrane underwater. The wetting equation for the solid–water–oil interface can be obtained by combining the Young’s equations for solid–air–water [51] and solid–air–oil interfaces, which was previously done by Jung and Bhushan [52]. The OCA in an aqueous medium $\gamma_{ow}$ can be calculated using the following equation [52]:

$$\cos \theta_{ow} = \frac{\gamma_{OA} \cos \theta_O - \gamma_{WA} \cos \theta_W}{\gamma_{OW}}$$

(7)

where $\gamma_{OA}$, $\gamma_{WA}$ and $\gamma_{OW}$ are the interfacial tensions of the oil–air, water–air and oil–water interfaces, respectively, and $\theta_W$ and $\theta_O$ are the water and oil CAs, respectively, in air. Eq. (7) predicts that hydrophilic surfaces ($\theta_W < 90^\circ$) often exhibit underwater oleophobicity, whereas hydrophobic ($\theta_W > 90^\circ$) and oleophilic ($\theta_W < 90^\circ$) surfaces are usually oleophilic underwater. This theoretical analysis is consistent with the experimental results showing that the membrane was hydrophobic and underwater oleophilic in water at pH 6.5. As previously discussed, the $\theta_{ow}$ value, which is the OCA of the SNP/DA-TiO$_2$/PI nanofibrous membrane in water, was measured to be $161.5^\circ$ at pH 12. Hence, based on Eq. (7), the surface was expected to be oleophobic with $\theta_O > 90^\circ$ because $\gamma_{OW} > \gamma_{WA}$ and $\theta_W < 90^\circ$. In fact, the surface must be oleophobic to successfully separate oil and water because it would prevent the oil from permeating the membrane after all the water passes through it.

To further understand the pH-induced oil-water separation process, the water and oil wetting processes are modeled in Fig. 8. Generally, an intrusion pressure, $\Delta P$, must be overcome before a liquid can wet the pore bottom because the advancing contact angle $\theta_A$ must be exceeded. This pressure is described by the following equation [53]:

$$\Delta P = \frac{2 \gamma}{R} = \frac{\rho \cos \theta_A}{A}$$

(8)

where $\gamma$ is the surface tension, $R$ is the meniscus radius, $\rho$ is the pore perimeter, $A$ is the pore area, and $\theta_A$ is the advancing contact angle on the membrane. Based on Eq. (8), when $\theta_A$ is greater than $90^\circ$, the membrane can withstand the intrusion pressure to some extent because $\Delta P > 0$. In this work, at pH 6.5, the membrane exhibited superhydrophilicity in water with a $\theta_W$ value that was apparently greater than $90^\circ$, which prevented water permeation through the membrane (Figs. 3a and g and 7a). In contrast, at pH 12, the membrane exhibited superhydrophilicity in water with a $\theta_W$ value of less than $90^\circ$. Therefore, based on Eq. (8), $\Delta P$ was negative, indicating that the water spontaneously passed through the membrane (Figs. 4a and f and 7b). After the permeation process, water was trapped in the spaces between the silica NPs and PI nanofibers, which might have enhanced the oil repulsion by...
the membrane and thus led to the observed superoleophobicity and high OCA (Fig. 7b, OCA > 90°). Then, the oil could not pass through the membrane after water permeation because \( \Delta P > 0 \) (Fig. 7c). Based on this analysis, the membrane exhibited a pH-induced change in the water permeability (from pH 6.5 to pH 12, for example). More importantly, the oil was retained by the membrane after water permeation due to the underwater superoleophobicity of the membrane at pH 12 (see Figs. 4f and 5b).

3.5. Oil-water separation performance

The performance of the as-prepared electrospun SNP/DA-TiO₂/PI nanofibrous membrane in oil-water separations was studied in detail using various model oil-water mixtures. Fig. 8 shows the permeate fluxes and separation efficiencies of the SNP/DA-TiO₂/PI nanofibrous membrane in the in-house built separation setup obtained for water mixtures with various oils, e.g., DCE, trichloromethane, carbon tetrachloride, dichloromethane and bromobenzene. The fluxes of the tested oil-water mixtures were found to be significantly higher than those obtained with commercial filtration membranes. The maximum flux of 6500 ± 100 L m\(^{-2}\) h\(^{-1}\), which was observed for a DCE-water mixture, is approximately 30 times higher than those achieved with commercial filtration membranes (20–200 L m\(^{-2}\) h\(^{-1}\) [54]). In addition, the flux only fluctuated and decreased slightly over 20 separation cycles, indicating that the nanofibrous membrane was highly stable and reusable (Fig. 8c). The high flux through and excellent stability of the nanofibrous membrane were attributed to its optimal pore size and PSD, as demonstrated by the N\(_2\) adsorption-desorption results. As shown in Fig. S11, the SNP/DA-TiO₂/PI membrane exhibited a type IV N\(_2\) adsorption-desorption isotherm. This membrane had mesopores of approximately 10–100 nm (mean size of ~50 nm) and a pore volume of 0.02346 cm\(^3\) g\(^{-1}\), indicating the presence of many pore channels that could enhance the gravity-driven liquid transport through it.

In addition to the flux, the membrane separation efficiency in oil-
water separation was also investigated. As shown in Fig. 8b, the separation efficiency of the SNP/DA-TiO$_2$/PI membrane was higher than 99% for all the tested oil-water mixtures. Even after twenty separation cycles, the membrane separation efficiency was still higher than 98%, as shown in Fig. 8d. In addition, the oil concentrations of the water collected after separation by the modified membrane were less than 1 ppm over 20 separation cycles, further demonstrating its high separation efficiency (Fig. 9).

The effects of the SNP/DA-TiO$_2$/PI nanofibrous membrane thickness on the permeate flux and separation efficiency were evaluated using a
DCE-water mixture at pH 6.5 (Fig. 10). With increasing membrane thickness, the separation flux decreased significantly, whereas the separation efficiency remained constant. The decrease in the flux was attributed to the lower porosities of the thicker membranes (Fig. 10c).

The SNP/DA-TiO$_2$/PI membrane must be stable under extreme conditions for wide use in oil-water separations. Two types of high-temperature resistance tests were performed using the as-prepared membranes. Fig. 11a shows that the SNP/DA-TiO$_2$/PI membrane maintained its hydrophobicity at pH 6.5 after heating at temperatures of up to 120 °C in air. After calcination at temperatures of up to 250 °C for 10 min, the WCA (pH 6.5) on the membrane remained constant.

This high thermal stability is quite promising because this membrane could be used to effectively separate oil-water mixtures while the oil burns, which occurs during oil spills. In addition, the high temperature resistance of the SNP/DA-TiO$_2$/PI membrane would enable oil-fouled membranes to be regenerated by calcination, which would remarkably enhance their reusability.

The mechanical strength and abrasion resistance of the SNP/DA-TiO$_2$/PI nanofibrous membrane are also important factors in practical applications. The stress-strain curves of the PI membrane in Fig. 12a show that it fractured at a high tensile stress of 400 MPa. This stress is high enough for the membrane to be suitable for use in self-supporting oil-water separations. Sandpaper abrasion tests were also performed to investigate the abrasion resistance of the SNP/DA-TiO$_2$/PI nanofibrous membrane (Figs. 12b and c and S12). WCA data collected at pH 6.5 after the abrasion tests (Fig. 12d) revealed a decrease in the WCA from 161.5° to approximately 147.7° after one abrasion cycle; however, the WCA remained constant after additional abrasion cycles. No visible damage to the membrane internal space was observed by SEM (Fig. S13) and high flux and separation efficiency were obtained (Fig. S14) after five sandpaper abrasion cycles.

4. Conclusions

A polyamide nanofibrous membrane (SNP/DA-TiO$_2$/PI) with pH- and ammonia-vapor-responsive surface wettability was designed and fabricated by electrospinning and solution dip-coating. High-strength electrospun PI nanofibers were used as the membrane matrix, and the membrane surface was modified to make it superhydrophobic and superoleophobic for use in oil-water separations. At pH 12 or higher, the DA-modified membrane surface became superhydrophilic and underwater superoleophobic, demonstrating its pH-responsive wettability. Moreover, water could permeate the membrane in oil-water separation under these conditions. The surface wettability transition was also induced by exposure to ammonia vapor, indicating that it might be possible to remotely control the membrane surface properties and hence oil-water separation. The flux and separation efficiency of this ‘smart’ nanofibrous membrane in oil-water separation were measured for several model oil (organic liquid)-water mixtures, and the results demonstrated its excellent separation properties and durability. Furthermore, tests performed under extreme conditions indicated that the dual-responsive membrane exhibited high thermal resistance and abrasion resistance, which are necessary for its use in practical applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2017.04.063.

References


