Fabrication of superhydrophobic electrospun polyimide nanofibers modified with polydopamine and polytetrafluoroethylene nanoparticles for oil–water separation

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ABSTRACT: The oil–water separation technologies of removing oil pollutants from water in an efficient and economical way is a challenge. The current methods used for oil–water separation suffer many shortcomings, including a low separation efficiency, complex separation equipment, high operation costs, and secondary pollution. In this study, we fabricated a highly flexible, high-intensity, quite stable superhydrophobic and superoleophilic polyimide (PI) nanofibrous membranes, which are much more efficient and cost efficient for oil–water separation by modifying the membranes with a polydopamine (PDA) solution and polytetrafluoroethylene (PTFE) dispersion. The fabricated membrane (PDA–PTFE–PI) possesses both the high tensile stress of PI and the superhydrophobic and superoleophilic properties of the PDA–PTFE coating. The modified membrane could separate various oil–water mixtures efficiently at a high flux (6000 L m⁻² h⁻¹) and an extremely high efficiency (>99%). Furthermore, even when the membrane was under an extremely hostile environment (with an ultrahigh temperature, strong acidity, or strong basicity), it still remained quickly stable with a good separation efficiency and recyclability after 10 cycles. We anticipate that our study will provide a new technology for the highly efficient mass production of oil–water mixture management.

KEYWORDS: electrospinning; membranes; recycling; separation techniques

INTRODUCTION

In recent years, oil-seepage accidents have happened frequently worldwide, and they have become a severe problem that must be taken into consideration. These accidents not only bring about a serious waste of oil resources but also cause irreversible damage to the natural environment; for example, the serious oil spill in Mexico in 2010¹–⁴ resulted in mass mortality of marine life. Hence, low-cost techniques that can efficiently separate oil–water emulsions or oil–water mixtures are necessary. To date, existing techniques for oil–water separation can be classified into the following categories: flotation, gravity separation, adsorption, ultrasonic separation, skimming, sedimentation under centrifugal fields, biological treatments, and electrocoalescence.¹³ However, most of them suffer from quite a number of drawbacks, including low separation efficiency, complex separation equipment, high operation costs, and secondary pollution. Membrane-based separation has proven to be an attractive and efficient method for oil–water separation as it has lower energy costs and higher separation efficiency.¹⁴

Inspired by the unique properties of lotus leaves,¹⁵–¹⁷ researchers have found that materials with special wettability toward oil or water have good application prospects in the field of oil–water separation because of their special selectivity to water and oil. Researchers¹⁸,¹⁹ have found that a combination of low-surface-energy materials and a hierarchical microstructure can benefit the formation of superhydrophobic surfaces, in particular, materials...
with superhydrophobic surfaces for water (with a water contact angle >150°) and with superoleophilic surfaces for oil (with an oil contact angle <10°). However, when the surfaces are under opposite conditions, superhydrophilic surfaces for water have a water contact angle of less than 10°, and superoleophobic surfaces for oil have an oil contact angle greater than 150°. Nanometer-or micrometer-sized surfaces are conducive to further boosting the surface wettability of the materials to be superhydrophobic or superoleophobic.\textsuperscript{18,19}

Electrospinning has attracted much attention since it was invented in 1902.\textsuperscript{20} Electrospinning is an efficient and versatile technique with a simple operation that uses an electric field to fabricate nanofibrous membranes. The diameter of electrospun nanofibers ranges from a few nanometers to micrometers.\textsuperscript{21} Electrospun nanofibers have been widely used in industries such as controlled drug delivery,\textsuperscript{22,23} air filtration,\textsuperscript{24–26} and wound dressings.\textsuperscript{27,28} A significant feature of electrospun nanofibers is their high specific surface areas, which can exactly meet the requirement of oil–water separation. Additionally, electrospun nanofibrous membranes have a large porosity, flexible surface functionalities, and high permeability to liquid; these membranes are also conducive to the application of oil–water mixture separation. However, although the electrospun membranes have been proven to have good performances for oil–water separation, some disadvantages, such as a poor mechanical stability\textsuperscript{29,30} and low breakthrough pressure, always limit their applications.\textsuperscript{31–33}

In this article, we report on the use of polyimide (PI) unexceptionable mechanical properties\textsuperscript{34,35} as an electrospun polymer for fabricating fiber membranes to separate oil–water mixtures. Highly flexible, chemically stable, high-flux electrospun PI nanofibrous membranes with a high mechanical tensile strength were fabricated in this study. The PI nanofibers membranes were modified with a polydopamine (PDA) and polytetrafluoroethylene (PTFE) dispersion; this resulted in an excellent superhydrophobic, superoleophilic surface. The results show that polyamide nanofiber membranes are promising for simple gravity-driven oil–water separation.

**EXPERIMENTAL**

**Materials and Solvents**
P-Phenylenediamine and 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA) were brought from Shanghai Aladdin Industrial Corp. and Changzhou Sunlight Pharmaceutical Co., Ltd., respectively. Before used, these were sublimated in 150 and 250 °C under reduced pressure. All of the solvents and reagents were analytically pure and were used without any other purification unless otherwise stated. N,N-Dimethyl acetamide (DMAc), dichloromethane (DCM), trichloromethane, tetrachloromethane, 1,2-dichloroethane (DCE), bromobenzene, aqueous ammonia, EtOH, and acetone were obtained from Nanjing Chemical Reagent Co., Ltd. Hexadecyltrimethylammonium bromide and 3-hydroxytyramine hydrochloride (dopamine hydrochloride) were purchased from Shanghai Aladdind Industrial Corp. A waterborne PTFE dispersion (solid content = 60%) was purchased from Guangdong Mingde Plastic Industrial Corp.

**Synthesis of Polyamide Acid (PAA)**
PAA was synthesized through low-temperature ring-opening polyaddition of BPDA and p-phenylene diamine as described in our previous report: solid BPDA (0.01 mol), p-phenylene diamine (0.01 mol), and 40 mL of DMAc were added to the three-necked flask in sequence with mechanically stirred vigorously at −5 °C under nitrogen. The reaction proceeded overnight and was then terminated by exposure to air and stored under refrigeration. The molecular weight distribution of PAA was measured by gel permeation chromatography (GPC; Agilent Technologies, Germany).

**Electrospinning of the PAA Nanofibrous Membrane and Imidization**
PAA was dissolved in DMAc at room temperature to obtain a 3 wt % electrospinning solution under magnetic stirring. Then, 0.1 wt % cetrimonium bromide was added to improve the electrical conductivity of the solution. Electrospinning was performed with an FM1206 electrospinning instrument (Beijing Future Material Sci-Tech, China). The ideal electrospinning parameters were found to be: feed rate = 1.5 mL/h, collector distance = 10 cm, and applied voltage = 25 kV (+15, −10 kV). The electrospinning apparatus is shown in Scheme 1. We performed the thermal imidization process by heating the PAA membranes according to the following protocol: 150 °C for 1 h, 200 °C for 1 h, 250 °C for 1 h, 300 °C for 1 h, 350 °C for 3 h, and 380 °C for 30 min.

**Preparation of the PDA–PTFE–PI Modified Membranes**
A volume of 0.40 mL of 28–30 wt % ammonia aqueous solution (NH\textsubscript{3}OH) was added to 100 mL of and EtOH/H\textsubscript{2}O mixture (3:7 v/v). Then, 0.2 g of dopamine hydrochloride was subsequently added to the previous solution and stirred at room temperature until we obtained the PDA solution.\textsuperscript{36}

Acetone and distilled water were used to wash the PI membranes three times in sequence before the modification process, and the
membranes were then dipped into the prepared PDA solution for 12 h with vigorous stirring. After being dried at 60 °C in a vacuum oven for 30 min, the PDA-coated PI membrane was prepared. The following procedure was used to add the PTFE nanoparticle dispersion to the PDA-coated PI membranes at room temperature for 4 h with vigorous stirring. Then, the membranes were dried in a vacuum oven at 60 °C again. After these treatments, the PI membranes were fully modified by the PDA–PTFE coatings.

**Instrumentation and Characterization**

The surface morphology of the modified PI membranes was characterized with scanning electron microscopy (SEM; S-4800, Hitachi, Ltd., Japan). The electrospun PDA–PTFE–PI membranes were prepared with an electrospinning instrument (Future, FM1206, Beijing, China). Then, the stress–strain curves for the PI sample were measured by a universal material testing machine (Sans, UTM6502, Shenzhen, China) at room temperature. The roughness of the membranes were measured by atomic force microscopy (Dimension Edge, Bruker, Germany) in tapping mode. Thermogravimetric analysis was performed on the PI membranes at a rate of 10 °C/min under a dynamic nitrogen flow with a TA Instruments 50, and the porosity and surface area of the nanofibers were studied with the Brunauer–Emmett–Teller and Barrett–Joyner–Halenda models via nitrogen adsorption and desorption measurement isotherms with an Autosorb-1 MP sorption instrument (QuanChrom). The X-ray diffraction analysis experiment was performed with a Rigaku Ultima IV (Japan) at a scanning rate of 5°/min.

**Free Oil–Water Mixture Separation Experiments**

We designed a homemade device for the separation test of the oil–water mixture; the device consisted of a flange, retort stands, two glass tubes, beakers, and modified membranes. The as-prepared membranes were fixed between the two glass tubes (diameter = 15 mm) by the flange. Then, a mixture of 10 mL of water labeled in methylene blue dye and 10 mL of oil labeled in red dye was prepared in a bottle by ultrasonication [Figure 4(a), shown later]. All of the data were measured three times and averaged.

The evaluation of the modified PI membrane separation efficiency ($E_{np}$) was calculated with eq. (1):

$$E_{np} = \frac{C_1}{C_0} \times 100\%$$

where $C_0$ and $C_1$ are the amounts of water before and after the separation process, respectively.

**RESULTS AND DISCUSSION**

**Characterization of the PDA–PTFE–PI Membranes**

Figure 1(a) is the SEM image of the pristine PI nanofibrous membranes. The diameter of the nanofibers was about 300 nm on average. After treatment with the PDA solution, the surface morphology of the PI nanofibers was obviously changed. There was a thin PDA layer covered in the solution, as shown in Figure 1(b). As described previously, the wettability of the surface was influenced by both their chemical constitution and the surface physical structure. The low-surface-energy hydrophobic PTFE nanoparticles after treatment by the PTFE dispersion are clearly visible in Figure 1(c). The SEM images of the cross section of the modified PDA–PTFE–PI nanofibrous membranes are shown in Figure S2 (Supporting Information), and the thickness of the membranes was measured to be about 34 μm. The PTFE nanoparticles remarkably improved the surface roughness of the PI membranes and then improved the surface hydrophobicity, according to the atomic force microscopy images (Figure S1, Supporting Information). The roughness of the PI membranes increased from 11.9 to 18.1 nm after the modification of the PDA–PTFE coating; this was suitable for the separation of oil–water mixtures.

In addition to the surface roughness, $N_2$ adsorption–desorption isotherms were performed with the Brunauer–Emmett–Teller and Barrett–Joyner–Halenda models. As shown in Figure S3 (Supporting Information), typical mesopores were found in the PI membranes, with pore sizes ranging from 10 to 30 nm and a center size of about 20 nm (surface area = 14.661 m²/g); this means the PDA–PTFE–PI membranes possessed superior properties for oil–water separation.

Fourier transform infrared (FTIR) spectra were used to analyze whether the PDA and PTFE particles were successfully modified on the PI membrane. The chemical structures of the modified PI nanofiber samples were also recorded with a Nicolet 8700 FTIR spectrometer with 32 scans at room temperature. FTIR spectra of the pristine PI, PDA–PI, and PDA–PTFE–PI membranes are displayed in Figure 2. The peaks at 1720, 1770, and 1370 cm⁻¹ corresponded to the –COOH, –CONH, and C=–N stretching vibrations, respectively. After the PDA was modified on the PI membrane surface, some peaks appeared at 1615, 1271, and 1057 cm⁻¹; these corresponded to the C=–N, C–N, and O–H stretching vibrations, respectively, of PDA and suggested the formation of PDA on the PI membrane surface. In contrast, the peaks at 1211 and 1155 cm⁻¹ were attributed to the symmetric and antisymmetric stretching vibration absorption peaks of CF₃ in PTFE; this indicated that the PTFE particles were successfully adhered to the PI membrane.

**Wettability of the PDA–PTFE–PI Fibrous Membranes**

The surface wettability of the fabricated PDA–PTFE–PI membranes was measured with a contact angle instrument (JC2000D1, Shanghai Zhong Chen Digital Technic Apparatus Co., Ltd.) at room temperature. From the pictures in Figure 3(a), after the pristine PI membranes were modified with the PDA and PTFE dispersion, respectively, the surface wettability of the membranes changed obviously from 118.52 to 151.4°; this means the modification was successful and efficient. Figure 3(b) shows the snapshots of the water droplet (≈2 μL) on the membranes. The water contact angles were about 151°; this suggested that the surface of the PDA–PTFE–PI nanofibrous membranes was superhydrophobic and could repel water completely. Meanwhile, the fibers with a high water contact angle were able to remain over 30 min; this means that the superhydrophobicity was quite stable. With modification of the PTFE dispersion, the wettability of the PI membrane was superhydrophobic because of the coefficient results of the low-surface energy and hierarchical structure. Although the hierarchical microstructure–nanostructure resulted from the PDA and PTFE particles, the low surface energy was due to the presence of the long F-alkyl chains. In addition, as shown in
Figure 1(c), the surface morphology of PDA–PTFE–PI was a three-dimensional hierarchical structure with a composition of PTFE particles on the PI membrane. With respect to the oil contact angle, DCE and n-hexane were used as the model heavy oil (with a density higher than that of water) and light oil (with a density lower than that of water), respectively. In air, the oil contact angle was approximately 0°, as determined by measurement with an n-hexane droplet (2 μL). The droplet completely was absorbed by the membrane within 1 s; this proved that the modified PI membranes were superoleophilic [Figure 3(c)]. The underwater oil contact angle was measured with a DCE droplet [Figure 3(d)]. The oil in water was quickly absorbed by the PDA–PTFE–PI nanofibrous membranes in 1 s. We concluded that the modified PDA–PTFE–PI membranes had a good ability to absorb the oil in water and would have important applications for the oil–water separation process. Next, we discuss the performance of the PDA–PTFE–PI membranes in the oil–water separation process.

Oil–Water Separation Performance
First, a series of oil–water mixtures (50% v/v) have been separated by our homemade separation setup [Figure 4(b)]; these included DCE, trichloromethane, carbon tetrachloride, DCM, and bromobenzene. In terms of the oil–water separation testing process, the maximum flux of the PDA–PTFE–PI nanofibrous membranes was about 6000 L·m⁻²·h⁻¹ for a separation of DCE–water mixture (Figure 5). They highly outperformed reported commercial filtration membranes with fluxes of 20–200 L·m⁻²·h⁻¹. Most importantly, as shown in Figure 5, the membranes presented an excellent separation ability for all of these oil–water mixtures, with an efficiency of nearly 100%. The flux and separation efficiency were both key parameters in evaluating the separation of the oil–water mixture. A high flux indicated that a membrane could deal with a larger volume of an oil–water mixture at the same time, whereas a high separation efficiency enabled the oil or water to be used in production without further treatment after the separation process. These results indicate that the fabricated PDA–PTFE–PI membranes could be used for the generic treatment of different types of oil–water mixtures.

Stability of the PDA–PTFE–PI Fibrous Membranes
The stabilities of the superhydrophobicity and superoleophilicity of the PDA–PTFE–PI nanofibrous membrane are highly critical for their practical application during the oil–water separation process.
process. Figure 6 shows the separation ability of the PDA–PTFE–PI nanofibrous membrane after 10 continuous cycles for the DCM–water mixture. Then repeated uses of the membrane had no any effect on the separation efficiency [Figure 6(a)], flux, or separation efficiency [Figure 6(b)].

Furthermore, the modified PDA–PTFE–PI membranes processed good thermogravimetric stability (Figure S4, Supporting Information). The thermogravimetric analysis of the PDA–PTFE–PI membrane showed that it decomposed at a temperature above 213 °C. Between 213 and 362 °C, its weight loss was 8% because
of the decomposition of the PDA–PTFE coating, whereas the melting points of PDA and PTFE were 220 and 327 °C, respectively. Figure S5 (Supporting Information) shows the X-ray diffraction patterns of the modified PDA–PTFE–PI membranes before and after the oil–water separation procedure. According to ref. 45, we calculated the relative crystallinity ($X_{cw}$) with eq. (2):

$$X_{cw} = \frac{I_c}{I_c + I_w} \times 100\%$$

(2)

where $I_c$ is the intensity of the crystalline peak and $I_w$ is intensity of the amorphous peak. From the X-ray diffraction results, each peak width was smaller than $3 \degree$, so we considered that there was no amorphous peak in the PDA–PTFE–PI membranes. This means that $I_w$ was zero. So, theoretically, $X_{cw}$ of the membranes was 100%, as determined with calculations both before and after the modification. This indicated that our membrane was very stable after the separation and could be repeatedly reused. Figure S6 (Supporting Information) shows the stress–strain curves of the PDA–PTFE–PI membrane. The tensile stress of the PI and modified PI membranes reached 240 MPa; this was rather high to make sure the membrane was flexible for oil–water separation process without any substrate.

To consider the effects of its use in a real, harsh environment, we tested the stability of the PDA–PTFE–PI membrane in a high-temperature environment with a large range. First, the resistance to high temperatures was characterized by the measurement of the water contact angle while the membrane was heated up to 120 °C. The water contact angle as a function of the temperature is shown in Figure 7(a). Moreover, the high-temperature resistance would
be remarkably enhanced the reusability by calcining the membrane to remove oil fouling. We determined the chemical stability by changing the environmental pH from 1 to 13. As shown in Figure 7(b) (pH = 7), the water contact angle was maintained at more than 120 °C toward a broad of pH 1–13; this showed its perfect stability under harsh conditions. When the temperature rose to 130 °C, these was an obvious drop. As far as we are concerned, the PDA coating was damaged at high temperature; this weakened the superhydrophobicity of the membranes (Figure S4, Supporting Information). These results indicate that the stability of the PDA–PTFE–PI membrane has the great potential to work in a harsh environment at high temperatures and within a large pH range.

**CONCLUSIONS**

In summary, we fabricated a highly flexible, highly superhydrophobic and superoleophobic PI nanofibrous membrane by modification with a PDA solution and PTFE dispersion. The PDA–PTFE–PI membrane possessed both the high tensile stress of PI and the superhydrophobic and superlipophilic properties of the PDA–PTFE coating. The modified membrane efficiently separated various oil–water mixtures both with a high efficiency (>99%) and a high flux (6000 L·m⁻²·h⁻¹). Furthermore, the fabricated PDA–PTFE–PI membrane was rather stable under an extremely hostile environment (with an ultrahigh temperature, a strong acidity, and a strong basicity) and still retained a good separation efficiency and recyclability after 10 cycles. Furthermore, as our approach was rather simple, cost-effective, and at room temperature work, it has wonderful potential applications for oil–water separation.

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**AUTHOR CONTRIBUTION**

Z. Liu and W. Ma contributed equally to this work.

**REFERENCES**


**Figure 7.** Water contact angles of the PDA–PTFE–PI membranes: (a) different pH values of the water in the oil–water mixtures and (b) heating at different temperatures. [Color figure can be viewed at wileyonlinelibrary.com]


