Confined interfacial polymerization of polyamide-graphene oxide composite membranes for water desalination

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ARTICLE INFO

Keywords:
- Graphene oxide
- Polyamide
- Confined interfacial polymerization
- Water purification
- Reverse osmosis

ABSTRACT

The developments of efficient reverse osmosis (RO) membranes and their fabrication mechanisms are significant for water purification. Graphene oxide (GO) membranes show excellent stability and large permeance, but the large transport nanochannels make it difficult to be applied for RO desalination. Herein, a strategy, confined interfacial polymerization, is reported for preparing ultrathin polyamide (PA)-GO membranes with excellent performance in RO desalination. By making use of the adsorption of negatively charged GO with oxygen-containing groups to meta-phenylene diamine (MPD), the polymerization between MPD and trimesoyl chloride (TMC) at void regions of GO layer is carried out, which can refine the size of transport nanochannels. The resulting PA-GO membrane displays high salt rejection of 99.7%. Because of the 30-nm thickness of and the small amount of formed PA, the large permeance of 3.0 L m⁻² h⁻¹ bar⁻¹ is achieved. Moreover, the PA-GO membrane shows good long-term stability, high chemical stability and low fouling propensity.

1. Introduction

The scarcity of clean and safe water becomes a critical issue as growth of population and progress of industrialization [1]. Desalination by membrane-based reverse osmosis (RO) is an energy-efficient technology for obtaining fresh water from seawater, brackish water and wastewater [2]. Most commercial RO membranes are fabricated by depositing polyamide (PA) selective layers on porous substrates [3]. PA selective layers of RO membranes for salt rejection are traditionally synthesized by interfacial polymerization, through immersing porous substrates (usually polysulfone-PSF) with impregnated meta-phenylene diamine (MPD) aqueous solution into trimesoyl chloride (TMC) organic solution [4,5]. The dense PA layers can be formed at the immiscible water/organic interfaces. As the results of the protruding MPD solution, the formed membranes usually have leaf-like structure, which enhances the surface roughness and then increases fouling propensity. Although PA membranes exhibit superior permeability and salt rejection than first-generation cellulose acetate membranes, their chlorine sensitivity and fouling propensity are bottlenecks for better practical application [6–13]. Moreover, development of efficient membranes to break through the limitation of trade-off between permeability and rejection is still the main research interest.

Graphene and its derivatives including graphene oxide (GO) and reduced graphene oxide (rGO), have great advantages for various applications because of their unique properties such as large surface area, excellent thermal and mechanical stability, high electrical and thermal conductivity [14–21]. These properties make it an attractive alternative material for RO membranes. In this study, we report a simple and efficient confined interfacial polymerization method for preparing ultrathin PA-GO membranes, and thus a high-performance RO membrane is obtained.
applications and for fabricating the separation membranes with excellent chemical stability and large permeance [14–20]. There are two main separation mechanisms of graphene-based membranes, separation by interlayered nanochannels and by transport through defects and pores. For mono-layered and few-layered graphene-based membranes, the artificial pores in graphene or intrinsic defects of GO and rGO are main molecular transport nanochannels. The pore size of defects determines the permselectivity for various molecules [21–27]. The single-layered graphene with subnanometer-sized pores created by oxygen plasma etching can reject salts totally [21]. However, controlling of the pores and scaling up of those membranes are extremely untoward. Meanwhile, the mechanical strength of those membranes is relatively poor. In stacked graphene-based membranes, usually including GO and rGO membranes, with thickness from tens of nanometers to several micrometers, the interlayered spacing between nanosheets are main nanochannels for molecular transport and separation [28–31]. Definitely, the intrinsic defects of GO and rGO sheets also provide transport nanochannels when the membrane thickness is nanometer-sized [32]. Water crowding can prop open the transport nanochannels to approximately 10 Å, hence the stacked graphene-based membranes are usually employed for loose nanofiltration rather than RO desalination [32–36]. Various methods have been proposed to adjust the nanochannels of stacked graphene-based membranes [37–43], but the application of graphene-based membranes in RO for salt rejection remains a great challenge.

Herein, we report a strategy, confined interfacial polymerization, for obtaining PA-GO membranes with excellent performance in RO desalination (Fig. 1). By filtration of MPD solution through ultrathin GO membranes, the negatively charged GO with oxygen-containing groups adsorbs MPD molecules. Then confined interfacial polymerization between MPD and TMC at void regions is carried out to refine the size of transport nanochannels. The PA-GO membranes thus prepared have thickness smaller than 30 nm and exhibit impressive NaCl rejection and permeance. Moreover, the prepared PA-GO membranes also show superior chemical stability in chlorine exposure, good antifouling property to bio-pollutants and long-term stability.

2. Experimental

2.1. Materials

The natural graphite flakes with size of 500 meshes were purchased from XFnano chemical Co., Ltd., China. KMnO₄, NaNO₃, meta-phenylene diamine (MPD), trimesoyl chloride (TMC), n-hexane, bovine serum albumin (BSA), sodium hypochlorite and other reagents used in this work were purchased from Kutai Chemical Reagent Co., China. Polysulfone ultrafiltration membrane with molecular weight cutoff of 50 kDa and mixed cellulose ester membrane with pore size of 0.22 μm were obtained from Liangwen Chemical Reagent Co., China. The reagents were used without further purification.

2.2. Synthesis of graphite oxide

Natural graphite flake (2.0 g) and NaNO₃ (1.0 g) were added gradually into concentrated H₂SO₄ (46 mL) with ice bath. KMnO₄ (6.0 g) was added slowly to the above suspension. In this process, the temperature was controlled below 20 °C. After reaction for 2 h in ice bath, the temperature of suspension was increased to 35 °C, and maintained for 1 h. Water (96 mL) was added into suspension slowly, and the temperature of suspension was increased to 98 °C and kept for 40 min. The prepared suspension was treated by 30% H₂O₂ solution. Ultimately, the product was washed by diluted HCl solution, collected and dried.

![Fig. 1. Schematic illustration of PA-GO membrane formation via confined interfacial polymerization.](image-url)
2.3. Preparation of PA-GO membrane

GO suspension with concentration of 1.0 mg/mL was prepared by ultrasonic exfoliation, and diluted to 2 μg/mL, 4 μg/mL and 8 μg/mL for obtaining GO membranes with different loading. GO membrane was fabricated by vacuum filtration of the diluted GO suspension (10 mL) on microfiltration substrate (mixed cellulose ester membrane with pore size of 0.22 μm). For synthesis of PA-GO membrane, MPD aqueous solution (1.00 w/v‰, 20 mL) was filtraited through the GO membrane and microfiltration substrate (for comparison) totally, and TMC n-hexane solution (0.05 w/v‰, 20 mL) was poured on the GO membrane and microfiltration substrate and maintained for 5 min. After polymerization, the prepared membrane was washed by n-hexane and dried. For obtaining the free-standing membrane, the PA-GO membrane was placed on water carefully. The PA-GO layer would float on water spontaneously. For characterization, the free-standing PA-GO layer was transferred on mica plate.

Fig. 3. Top view and cross-sectional view SEM images of (a,b) the GO membrane and (c,d) the PA-GO membrane. Optical images of (e) the GO membrane and (f) the PA-GO membrane. (g) The dynamic contact angle of the PA-GO membrane. The GO and PA-GO membranes were prepared with GO loading of 80 μg.
2.4. Preparation of PA/PSF membrane

PA/PSF membrane was synthesized by typical interfacial polymerization of MPD and TMC. PSF ultrafiltration membrane with molecular weight cutoff of 50 kDa was first cleaned by water and fixed in vacuum filtration device without suction. MPD aqueous solution (2.0 wt %, 10 mL) was added and kept for 5 min. After removing the excess MPD solution, TMC organic solution (0.1 wt%, 10 mL) was poured on the ultrafiltration membrane for polymerization. After reaction for 5 min, the prepared membrane was washed by n-hexane and dried.

2.5. Characterization

Membrane morphology was characterized by a scanning electron microscope (Ultra-55, Zeiss Co.) with accelerating voltage of 5 kV. To reduce charging effect, an ultrathin gold layer was coated on samples by using an ion coater. Chemical structure was studied by a Fourier transform infrared spectrophotometer (IRTracer-100, Shimadzu Co.). Surface morphology was investigated by using an atomic force microscope (Bioscope Catalyst Nanoscope-V, Bruker, USA). The sample was fixed on a mica plate for measurement. Water contact angle of membranes was observed by a Data Physics Instrument (OCA20/data-physics, Germany). A tensile test instrument (WTD-5, Shanding Huace, China) was employed to measure the tensile strength of membranes. X-ray photoelectron spectroscopy (XPS) experiment was carried on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer).

2.6. Separation performance

The desalination performance of the prepared membranes was evaluated by a dead-end filtration system with effective area of 7.0 cm². The experiment was carried out with feed pressure of 10 bar and NaCl solution with concentration of 2.0 g L⁻¹ at ambient temperature. To reduce the effect of concentration polarization, the feed solution was stirred constantly. After running stably, performance data were read and recorded. NaCl concentration was measured by a conductivity meter. The permeance of pure water and MPD solution through GO membranes with different GO loadings was studied by vacuum filtration directly. For studying the long-term stability, a cross-flow filtration system with effective area of 7.0 cm² and pressure of 8 bar was employed for desalination. The data were read and recorded after running stably. Measurements were repeated three times each, for three samples.
and averaged. The permeance ($P$) with unit of $L \, m^{-2} \, h^{-1} \, bar^{-1}$ was calculated by permeate volume ($V$), permeate time ($t$) and feed pressure ($\Delta p$). Rejection ($R$) was calculated by the salt concentration of the feed solution ($C_f$) and the permeate solution ($C_p$).

$$P = \frac{V}{At \Delta p}$$

$$R = \left(1 - \frac{C_f}{C_p}\right) \times 100\%$$

2.7. Fouling property

Fouling property of membranes was also investigated by the cross-flow filtration system with effective area of 7.0 cm$^2$. Filtration was first carried out with pure water (1000 mL) at pressure of 8 bar. Then bovine serum albumin (BSA, 0.1 g) was added into feed. The permeance data was monitored at 1 h intervals. After running for 12 h, the cleaning pure water was employed to flush the membranes for removing the foulant. Then fresh water (1000 mL) was used to replace the cleaning water to evaluate the recovery. The normalized permeance was calculated through dividing the real-time permeance by the initial one.

2.8. Chlorine stability

The membrane was fixed in a dead-end filtration system as described in separation performance. Sodium hypochlorite solution with concentration of 5.0 g L$^{-1}$ was poured in the feed container and contacted directly with the feed side of membrane for different times. After exposure for different times, sodium hypochlorite solution was removed. The feed container and the exposed PA-GO membrane or PA/PSF membrane were rinsed thoroughly by water prior to filtration. Then NaCl rejection of the PA-GO membrane or the PA/PSF membrane was studied for illustrating the chlorine stability of membranes.

3. Results and discussion

3.1. Membrane synthesis

Graphite oxide was fabricated by modified Hummers method, and exfoliated in water by ultrasonic treatment for obtaining the GO suspension [44,45]. The GO membranes were prepared via depositing the GO sheets on microfiltration membranes with pore size of 0.22 $\mu$m by vacuum filtration. For synthesizing the PA-GO membranes, MPD aqueous solution was filtrated through the GO membranes, and TMC n-hexane solution was poured on the GO membranes for polymerization. Because of the negatively charges and small interlayered spacing of GO membranes, MPD molecules were trapped through electrostatic interaction and molecular size effect. Since the oxygen-containing groups of GO could reacted with the amino group of MPD, the interlayered spacing of GO membranes was narrowed, [39] thereby leading to the much smaller permeance of GO membranes for MPD solution than pure water (Fig. 2). As the increase of GO loading, the reduction in permeance became larger. Because the GO membranes provided defined interfaces and reduced the release of MPD molecules, the polymerization could be controlled effectively. This confined interfacial polymerization
prevented the protruding of MPD solution from substrates to TMC solution, which would lead to rough membrane surfaces and generally occurred in traditional interfacial polymerization [46,47]. Moreover, the oxygen-containing groups, which usually caused negatively charges, mostly located at edges and defects of GO sheets [32]. These regions adsorbed more amino-contained MPD molecules. Meanwhile, the edges and defects of GO in the top layer of membranes were main molecular transport nanochannels for release of the adsorbed MPD molecules. Taking consideration of above factors, PA would preferentially grow on edges and defects of GO sheets, thereby controlling the size of nanochannels and improving salt rejection.

3.2. Membrane characterization

Fig. 3 presents SEM images of the substrate, the GO membrane with GO loading of 80 $\mu$g (equal to 64 mg m$^{-2}$) and the PA-GO membrane with GO loading of 80 $\mu$g. It was obvious that there continuous GO layer and PA-GO layer covered on substrates. Compared with the GO membrane, the PA-GO membrane had fewer wrinkles and its brown color became darker after confined interfacial polymerization. As expected, unlike the membranes prepared by traditional polymerization, there no leaf-like structure was observed in the PA-GO membrane. The PA-GO membrane with thickness of about 30 nm was slightly thicker than the GO membrane (Fig. 3d). The optical images indicated the GO and PA-GO layers covered on substrates uniformly (Fig. 3e,f). Fig. 3g displays the dynamic contact angle of the PA-GO membrane. The membrane showed relatively large contact angle of about 85°, which reduced with extension of time. This should be attributed to that the hydrophilic edges and defect regions of GO with polar oxygen-containing groups were preferentially coated by PA and the hydrophobic regions of GO were selectively exposed during contact angle measurement. The chemical structures of the substrate, the GO membrane and the PA-GO membrane were characterized by ATR-FTIR (Fig. 4a,b). The characteristic peak of C–O bond in spectra of the GO membrane and the PA-GO membrane was more intense than that of in substrate spectrum due to the deposited GO sheets [48]. After polymerization, the characteristic peaks at 1540 cm$^{-1}$ for C–O bond of amide and 1660 cm$^{-1}$ for C–N bond of amide in spectrum of the PA-GO membrane occurred [49]. Although the intensity was weak due to the small amount of the formed polymer, this still demonstrated the formation of PA layer. For further confirming the polymerization, XPS was employed to characterize the chemical structure of the PA-GO membrane (Fig. 4c,d). The surface of the PA-GO membrane was mainly composed of four elements of carbon (75.5%), nitrogen (10.8%), oxygen (13.4%) and chlorine (0.3%). The narrow Cls spectrum showed five peaks at 284.5 eV (C–H, C–C and C=C), 285.2 eV (C–CONH and C-COOH), 285.8 eV (C–N), 287.8 eV (N–C=O) and 288.4 eV (O–C=O) [50]. These results demonstrated the successful polymerization of PA again. The mechanical stability of the membranes was tested. The tensile stress at break and elongation at break of the substrate (7.2 MPa, 5.5%), the GO membrane (7.4 MPa, 6.4%) and the PA-GO membrane (6.6 MPa, 4.8%) were similar. Since both GO and PA-GO layers were ultrathin, the mechanical strength was mainly provided by the substrates. We also synthesized the PA-GO membranes with different loadings. As shown in Fig. 5, the PA-GO membrane with GO amount of 40 $\mu$g was defect-free. However, when the GO amount was reduced to 20 $\mu$g, the formed GO layer possessed...
some large cracks due to the suction of vacuum filtration in preparation. After MPD solution filtration and polymerization, the deposited layer even had a fragmented structure. This was attributed to that the shear force from polymerization of PA destroyed the arrangement and structure of the ultrathin GO membrane.

Interestingly, after putting the prepared membranes with GO loading of 80 μg on water, the PA-GO layer detached from substrate and floated on water, but the GO layer and substrate of GO membrane jointly sank into water. This phenomenon should be explained by wetting and surface tension. Because interlayered spacing of stacked GO provided capillary, water molecules passed through quickly and wetted whole GO membrane by capillary effect [51], thus the GO membrane sank into water. For the PA-GO membrane, although capillary effect existed in GO layer and substrate as well, low permeability of PA layer resisted the rapid wetting of whole membrane. The surface tension and gravity made the PA-GO layer separate from the substrate. The free-standing PA-GO membrane was transferred on mica plate for characterization. The PA side of the PA-GO membrane was relatively smoother than the GO side (Fig. 6). The GO side showed many embossments due to the unfixed GO sheets after water treatment and imprinting from the pores of substrates. Fig. 6 also displays that the PA side possessed some small bumps with diameter of 40–120 nm, but the GO side had not. The bump structure should be the result of preferential growth of PA through confined interfacial polymerization. The GO side had much better hydrophilic than PA side. Because of the embossing structure and the unfixed GO sheets, the contact angle of GO side was only 18°, which is even much smaller than those of the reported GO membranes [52]. On the contrary, the PA side displayed lower hydrophilicity with contact angle of 83°. Fig. 7 shows the results of AFM characterization. The AFM image and size distribution shows the small bumps with diameter of 60–80 nm. The edge image and height distribution indicates that the membrane thickness of about 30–40 nm (Fig. 7b,d).
3.3. Desalination performance

We evaluated the desalination performance of the prepared membranes via dead-end filtration. As shown in Fig. 8, with the increase of GO loading, water permeance and NaCl rejection decreased and increased, respectively. The PA membrane without GO deposition and the PA-GO membrane with low GO loading of 20 μg almost had no rejection for NaCl, because the excess influx of MPD solution from substrate to TMC solution and the quick polymerization of PA could not lead to the formation of dense PA layer. This was consistent with the membrane structure with large cracks as shown in SEM images (Fig. 5b). Yet the PA-GO membrane with GO loading of 80 μg showed high permeance of 3.0 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ and outstanding rejection of 99.7%. As well as the PA-GO membrane with GO loading of 40 μg exhibited large permeance of 4.0 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ and good rejection of 94.3%. The better rejection and relatively smaller permeance of the membrane with GO loading of 80 μg was explained by that the more MPD sorption promoted the formation of thicker and denser membrane. For comparison, PSF membrane with molecular weight cutoff of 50 kDa was employed to fabricate the PA/PSF membrane by traditional interfacial polymerization. The prepared PA/PSF membrane had permeance of 1.1 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ and rejection of 94.5%. Relatively, the PA-GO membranes prepared by confined interfacial polymerization had about triple to quintuple permeance and similar or even much higher rejection. Although the pure GO membrane with GO loading of 80 μg exhibited larger permeance than the PA-GO membranes, the rejection of only 10.4% was too small to RO application. We also tried to fabricate the PA-GO membranes though filtering MPD and GO mixture suspension followed by polymerization. But the prepared composite membrane displayed a low rejection of 82%. This may be because that MPD with amino group affected the arrangement of negatively charged GO to uniform layer, thus leading to poor interfacial polymerization. These results demonstrated that confined interfacial polymerization could fabricate defect-free, highly permeable and excellently selective RO membranes.

As analysis in previous study a reasonable desalination membrane would be possess permeance of 2−4 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ and as high as possible rejection [53]. That is to say that increasing the water-solute selectivity is more needed than improving permeance for practical applications. Compared with the RO membranes reported in previous studies, the PA-GO membranes prepared in this study showed superior separation performance, especially with higher rejection (Fig. 9) [6,10,12,13,47,49,54,55].

Long-term stability of membranes is critical for practical application. It should be noted, because of the hydrophilicity of GO sheets, GO membranes have the risk of re-dispersion in water, especially under the operation of cross-flow filtration. We investigated the desalination performance of the PA-GO membrane with GO loading of 80 μg by cross-flow filtration. The water permeance showed only small fluctuation in 5-day filtration, and the rejection was always greater than 99.7% (Fig. 10). This impressive performance demonstrated the excellent stability of the prepared PA-GO membrane.

3.4. Antifouling and chlorine resistant properties

Membrane fouling will degrade the desalination performance seriously. To illustrate the fouling behavior, water permeance of the PA-GO membrane with GO loading of 80 μg was studied by cross-flow filtration of BSA solution. Water permeance displayed reduction in first 2 h, and then reached a plateau. After filtration for 12 h, the permeance decline was 26.8%, which was smaller than 33.1% of the PA/PSF membrane (Fig. 11). Meanwhile, after simple hydraulic washing, the permeance of the PA-GO membrane showed higher recovery ratio than that of the PA/PSF membrane. These result demonstrated that the PA-GO membrane had better antifouling property. Surface roughness influences fouling behavior drastically. Larger roughness leads to more dead space and results in worse fouling. Since there was no leaf-like structure, the PA-GO membrane showed lower fouling propensity.

Poor chlorine resistance of RO membranes is another issue in practical application. We further studied the chemical stability of the PA-GO membrane. The PA-GO membrane with GO loading of 80 μg was treated by sodium hypochlorite solution for different times before filtration. The results are shown in Fig. 12. Because chlorine attack cause the cleavage of cross-linked PA network due to N-chlorination and ring chlorination reaction [56], the rejection of the prepared membranes decreased with the extension of exposure time. Compared with the PA/PSF membrane with drastic deterioration after exposure, which was also observed in previously reported PA membranes [8,9], the PA-GO membrane showed better chlorine resistance. This result may be attributed to that the GO sheets prevented the chlorine attack as protector and blocked the active radicals by electrostatic repulsion [13,54].
Moreover, the membranes displayed good chlorine resistance, low fouling propensity and excellent long-term stability. Besides the great potential of PA-GO membranes in desalination application, the design concept in this study may also provide a pathway to synthesize other molecular separation membranes.

**Acknowledgments**

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51708252), the Fundamental Research Funds for the Central Universities (Grant No. 21617322) and Jinan University (Grant No. 88016674).

**References**


