Contents lists available at ScienceDirect

# Desalination

journal homepage: www.elsevier.com/locate/desal

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



DESALINATION

Jiali Shi, Wufeng Wu, Yan Xia, Zhanjun Li, Wanbin Li\*

School of Environment, Guangzhou Key Laboratory of Environmental Exposure and Health, and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou 510632, PR China

GRAPHICAL ABSTRACT



# 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  $3.0 \text{ Lm}^{-2} \text{h}^{-1} \text{ bar}^{-1}$  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

E-mail address: gandeylin@126.com (W. Li).

https://doi.org/10.1016/j.desal.2018.04.030

Received 26 January 2018; Received in revised form 26 April 2018; Accepted 30 April 2018 Available online 09 May 2018 0011-9164/ © 2018 Elsevier B.V. All rights reserved.



<sup>\*</sup> Corresponding author.



Fig. 1. Schematic illustration of PA-GO membrane formation via confined interfacial polymerization.



Fig. 2. Permeance of pure water and MPD solution through the GO membranes with different loadings.

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 singlelayered 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.  $KMnO_4$ ,  $NaNO_3$ , 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  $\mu m$  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 NaNO<sub>3</sub> (1.0 g) were added gradually into concentrated  $H_2SO_4$  (46 mL) with ice bath. KMnO<sub>4</sub> (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%  $H_2O_2$  solution. Ultimately, the product was washed by diluted HCl solution, collected and dried.



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  $\mu$ g.

## 2.3. Preparation of PA-GO membrane

GO suspension with concentration of 1.0 mg/mL was prepared by ultrasonic exfoliation, and diluted to  $2 \mu \text{g/mL}$ ,  $4 \mu \text{g/mL}$  and  $8 \mu \text{g/mL}$  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  $0.22 \mu \text{m}$ ). For synthesis of PA-GO membrane, MPD aqueous solution (1.00 w/v‰, 20 mL) was filtrated 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. 4. (a,b) ATR-FTIR spectra of the microfiltration substrate, the GO membrane and the PA-GO membrane. (c,d) XPS spectra and high-resolution C 1 s spectra 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 Catylyst 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/dataphysics, 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 cm<sup>2</sup>. The experiment was carried out with feed pressure of 10 bar and NaCl solution with concentration of  $2.0 \,\mathrm{g \, L^{-1}}$  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 cm<sup>2</sup> 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



Fig. 5. SEM images of (a) the GO membrane with GO loading of 20 µg, (b) the PA-GO membrane with GO loading of 20 µg and (c,d) the PA-GO membrane with GO loading of 40 µg.

and averaged. The permeance (*P*) with unit of L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> was calculated by permeate valume (*V*), permeate time (*t*) and feed pressure ( $\Delta p$ ). Rejection (*R*) was calculated by the salt concentration of the feed solution (C<sub>*t*</sub>) and the permeate solution (C<sub>*p*</sub>).

$$P = \frac{V}{At\Delta p} \tag{1}$$

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}$$

#### 2.7. Fouling property

Fouling property of membranes was also investigated by the crossflow filtration system with effective area of  $7.0 \text{ cm}^2$ . 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 descried in separation performance. Sodium hypochlorite solution with concentration of  $5.0 \text{ g L}^{-1}$  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 µm by vacuum filtration. For synthesizing the PA-GO membranes, MPD aqueous solution was filtrated through the GO membranes, and TMC nhexane 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



Fig. 6. SEM images of (a,b) PA side and (c,d) GO side of the PA-GO membrane with GO loading of 80 µg on mica plate. The insets in (a,c) are the contact angles of PA side and GO side. The insets in (b,d) are SEM images with higher magnification.

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<sup>-2</sup>) 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  $1540 \text{ cm}^{-1}$  for C–O bond of amide and  $1660 \text{ cm}^{-1}$  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 C1s 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 amout of 40 µg was defect-free. However, when the GO amount was reduced to 20 µg, the formed GO layer possessed



Fig. 7. (a,b) AFM images of the PA-GO membrane on mica plate. (c) Grain size distribution and (d) height distribution of the PA-GO membrane on mica plate. The membrane was prepared with GO loading of 80 µg.



Fig. 8. Water permeance and NaCl rejection of the PA-GO membranes. The performance of the PA/PSF membrane, which was synthesized by traditional interfacial polymerization in this study, is displayed for comparison.

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).



Fig. 9. Comparison of the PA-GO membrane with other RO membranes reported in previous studies [6,10,12,13,47,49,54,55].



Fig. 10. Desalination performance of the PA-GO membrane prepared with GO loading of  $80\,\mu g$  as the function of times.

# 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  $3.0 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  and outstanding rejection of 99.7%. As well as the PA-GO membrane with GO loading of 40 µg exhibited large permeance of  $4.0 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  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  $1.1 \,\mathrm{Lm}^{-2} \mathrm{h}^{-1} \mathrm{bar}^{-1}$  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  $2-4 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  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  $80 \,\mu g$  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 influence 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  $80 \mu g$  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].



Fig. 11. Effect of BSA foulant on normalization permeance of the PA-GO membrane with GO loading of  $80 \,\mu g$ . The fouling property of the PA/PSF membrane, which was synthesized by traditional interfacial polymerization in this study, is displayed for comparison.



Fig. 12. Effect of chlorine exposure on NaCl rejection of the PA-GO membrane with GO loading of 80  $\mu g$ . The chlorine resistance of the PA/PSF membrane, which was synthesized by traditional interfacial polymerization in this study, is displayed for comparison.

#### 4. Conclusion

In conclusion, we have successfully fabricated the PA-GO membranes with excellent desalination performance by confined interfacial polymerization. By filtration of MPD solution through GO membranes, the negatively charged GO with oxygen-containing groups adsorbed MPD molecules. The confined interfacial polymerization of PA between adsorbed MPD and TMC at defects and edges of GO sheets refined the size of transport nanochannels, as well as the small thickness was 30 nm, the prepared PA-GO membrane showed outstanding NaCl rejection of 99.7% and large permeance of  $3.0 \, \text{Lm}^{-2} \, \text{h}^{-1} \, \text{bar}^{-1}$ .

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

- J.R. Werber, C.O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, Nat. Rev. Mater. 1 (2016) 16018.
- [2] A.G. Fane, R. Wang, M.X. Hu, Synthetic membranes for water purification: status and future, Angew. Chem. Int. Ed. 54 (2015) 3368–3386.
- [3] D. Li, Y. Yan, H. Wang, Recent advances in polymer and polymer composite membranes for reverse and forward osmosis processes, Prog. Polym. Sci. 61 (2016) 104–155.
- [4] A.K. Ghosh, B.H. Jeong, X. Huang, E.M.V. Hoek, Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties, J. Membr. Sci. 311 (2008) 34–45.
- [5] J. Yin, G. Zhu, B. Deng, Graphene oxide (GO) enhanced polyamide (PA) thin-film nanocomposite (TFN) membrane for water purification, Desalination 379 (2016) 93–101.
- [6] H.B. Park, B.D. Freeman, Z.B. Zhang, M. Sankir, J.E. McGrath, Highly chlorinetolerant polymers for desalination, Angew. Chem. Int. Ed. 47 (2008) 6019–6024.
- [7] R. Yang, H. Jang, R. Stocker, K.K. Gleason, Synergistic prevention of biofouling in seawater desalination by zwitterionic surfaces and low-level chlorination, Adv. Mater. 26 (2014) 1711–1718.
- [8] K.L. Cho, A.J. Hill, F. Caruso, S.E. Kentish, Chlorine resistant glutaraldehyde crosslinked polyelectrolyte multilayer membranes for desalination, Adv. Mater. 27 (2015) 2791–2796.
- [9] S. Surawanvijit, A. Rahardianto, Y. Cohen, An integrated approach for characterization of polyamide reverse osmosis membrane degradation due to exposure to free chlorine, J. Membr. Sci. 510 (2016) 164–173.
- [10] X. Huang, K.L. Marsh, B.T. McVerry, E.M.V. Hoek, R.B. Kaner, Low-fouling antibacterial reverse osmosis membranes via surface grafting of graphene oxide, ACS Appl. Mater. Interfaces 8 (2016) 14334–14338.
- [11] H.M. Hegab, A. ElMekawy, T.G. Barclay, A. Michelmore, L. Zou, C.P. Saint, M. Ginic-Markovic, Effective in-situ chemical surface modification of forward osmosis membranes with polydopamine-induced graphene oxide for biofouling mitigation, Desalination 385 (2016) 126–137.
- [12] H. Huang, S. Lin, L. Zhang, L. Hou, Chlorine-resistant polyamide reverse osmosis membrane with monitorable and regenerative sacrificial layers, ACS Appl. Mater. Interfaces 9 (2017) 10214–10223.
- [13] X. Song, Q. Zhou, T. Zhang, H. Xu, Z. Wang, Pressure-assisted preparation of graphene oxide quantum dot-incorporated reverse osmosis membranes: antifouling and chlorine resistance potentials, J. Mater. Chem. A 4 (2016) 16896–16905.
- [14] G. Liu, W. Jin, N. Xu, Graphene-based membranes, Chem. Soc. Rev. 44 (2015) 5016–5030.
- [15] K.A. Mahmoud, B. Mansoor, A. Mansour, M. Khraisheh, Functional graphene nanosheets: the next generation membranes for water desalination, Desalination 356 (2015) 208–225.
- [16] J. Zhu, M. Tian, J. Hou, J. Wang, J. Lin, Y. Zhang, J. Liu, B.V. Bruggen, Surface zwitterionic functionalized graphene oxide for a novel loose nanofiltration membrane, J. Mater. Chem. A 4 (2016) 1980–1990.
- [17] L. Yu, Y. Zhang, B. Zhang, J. Liu, H. Zhang, C. Song, Preparation and characterization of HPEI-GO/PES ultrafiltration membrane with antifouling and antibacterial properties, J. Membr. Sci. 447 (2013) 452–462.
- [18] M. Hosseini, Jafar. Azamat, H. Erfan-Niya, Improving the performance of water desalination through ultra-permeable functionalized nanoporous graphene oxide membrane, Appl. Surf. Sci. 427 ( (2018) 1000–1008.
- [19] P. Liu, T. Yan, L. Shi, H.S. Park, X. Chen, Z. Zhao, D. Zhang, Graphene-based materials for capacitive deionization, J. Mater. Chem. A 5 (2017) 13907–13943.
- [20] H. Duan, T. Yan, G. Chen, J. Zhang, L. Shi, D. Zhang, A facile strategy for the fast construction of porous graphene frameworks and their enhanced electrosorption performance, Chem. Commun. 53 (2017) 7465–7468.
- [21] S.P. Surwade, S.N. Smirnov, I.V. Vlassiouk, R.R. Unocic, G.M. Veith, S. Dai, S.M. Mahurin, Water desalination using nanoporous single-layer graphene, Nat. Nanotechnol. 10 (2015) 459–464.
- [22] T. Jain, B.C. Rasera, R.J.S. Guerrero, M.S.H. Boutilier, S.C. O'Hern, J.C. Idrobo, R. Karnik, Heterogeneous sub-continuum ionic transport in statistically isolated graphene nanopores, Nat. Nanotechnol. 10 (2015) 1053–1057.
- [23] D.C. Tanugi, J.C. Grossman, Mechanical strength of nanoporous graphene as a desalination membrane, Nano Lett. 14 (2014) 6171–6178.
- [24] S.C. O'Hern, D. Jang, S. Bose, J.C. Idrobo, Y. Song, T. Laoui, J. Kong, R. Karnik, Nanofiltration across defect-sealed nanoporous monolayer graphene, Nano Lett. 15

- [25] L.C. Lin, J.C. Grossman, Atomistic understandings of reduced graphene oxide as an ultrathin-film nanoporous membrane for separations, Nat. Commun. 6 (2015) 8335.
- [26] P.R. Kidambi, M.S.H. Boutilier, L. Wang, D. Jang, J. Kim, R. Karnik, Selective nanoscale mass transport across atomically thin single crystalline graphene membranes, Adv. Mater. 29 (2017) 1605896.
- [27] L. Wang, M.S.H. Boutilier, P.R. Kidambi, D. Jang, N.G. Hadjiconstantinou, R. Karnik, Fundamental transport mechanisms, fabrication and potential applications of nanoporous atomically thin membranes, Nat. Nanotechnol. 12 (2017) 509–522.
- [28] B. Mi, Graphene oxide membranes for ionic and molecular sieving, Science 343 (2014) 740–742.
- [29] R.K. Joshi, P. Carbone, F.C. Wang, V.G. Kravets, Y. Su, I.V. Grigorieva, H.A. Wu, A.K. Geim, R.R. Nair, Precise and ultrafast molecular sieving through graphene oxide membranes, Science 343 (2014) 752–754.
- [30] S. Safaei, R. Tavakoli, On the design of graphene oxide nanosheets membranes for water desalination, Desalination 422 (2017) 83–90.
- [31] Y. Long, K. Wang, G. Xiang, K. Song, G. Zhou, X. Wang, Molecule channels directed by cation-decorated graphene oxide nanosheets and their application as membrane reactors, Adv. Mater. 29 (2017) 1606093.
- [32] Y. Han, Z. Xu, C. Gao, Ultrathin graphene nanofiltration membrane for water purification, Adv. Funct. Mater. 23 (2013) 3693–3700.
- [33] H. Huang, Z. Song, N. Wei, L. Shi, Y. Mao, Y. Ying, L. Sun, Z. Xu, X. Peng, Ultrafast viscous water flow through nanostrand-channelled graphene oxide membranes, Nat. Commun. 4 (2013) 2979.
- [34] K. Goh, W. Jiang, H.E. Karahan, S. Zhai, L. Wei, D. Yu, A.G. Fane, R. Wang, Y. Chen, All-carbon nanoarchitectures as high-performance separation membranes with superior stability, Adv. Funct. Mater. 25 (2015) 7348–7359.
- [35] A. Akbari, P. Sheath, S.T. Martin, D.B. Shinde, M. Shaibani, P.C. Banerjee, R. Tkacz, D. Bhattacharyya, M. Majumder, Large-area graphene-based nanofiltration membranes by shear alignment of discotic nematic liquid crystals of graphene oxide, Nat. Commun. 7 (2016) 10891.
- [36] L. Huang, J. Chen, T. Gao, M. Zhang, Y. Li, L. Dai, L. Qu, G. Shi, Reduced graphene oxide membranes for ultrafast organic solvent nanofiltration, Adv. Mater. 28 (2016) 8669–8674.
- [37] L. Huang, Y. Li, Q. Zhou, W. Yuan, G. Shi, Graphene oxide membranes with tunable semipermeability in organic solvents, Adv. Mater. 27 (2015) 3797–3802.
- [38] H. Liu, H. Wang, X. Zhang, Facile fabrication of freestanding ultrathin reduced graphene oxide membranes for water purification, Adv. Mater. 27 (2015) 249–254.
- [39] W.S. Hung, C.H. Tsou, M.D. Guzman, Q.F. An, Y.L. Liu, Y.M. Zhang, C.C. Hu, K.R. Lee, J.Y. Lai, Cross-linking with diamine monomers to prepare composite graphene oxide-framework membranes with varying d-spacing, Chem. Mater. 26 (2014) 2983–2990.
- [40] Y. Yuan, X. Gao, Y. Wei, X. Wang, J. Wang, Y. Zhang, C. Gao, Enhanced desalination performance of carboxyl functionalized graphene oxide nanofiltration membranes, Desalination 405 (2017) 29–39.
- [41] L. Zhu, H. Wang, J. Bai, J. Liu, Y. Zhang, A porous graphene composite membrane

intercalated by halloysite nanotubes for efficient dye desalination, Desalination 420 (2017) 145–157.

- [42] W.L. Xu, C. Fang, F. Zhou, Z. Song, Q. Liu, R. Qiao, M. Yu, Self-assembly: a facile way of forming ultrathin, high-performance graphene oxide membranes for water purification, Nano Lett. 17 (2017) 2928–2933.
- [43] J. Abraham, K.S. Vasu, C.D. Williams, K. Gopinadhan, Y. Su, C.T. Cherian, J. Dix, E. Prestat, S.J. Haigh, I.V. Grigorieva, P. Carbone, A.K. Geim, R.R. Nair, Tunable sieving of ions using graphene oxide membranes, Nat. Nanotechnol. 12 (2017) 546–550.
- [44] W. Li, Y. Zhang, Z. Xu, A. Yang, Q. Meng, G. Zhang, Self-assembled graphene oxide microcapsules with adjustable permeability and yolk-shell superstructures derived from atomized droplets, Chem. Commun. 50 (2014) 15867–15869.
- [45] W. Li, Y. Zhang, P. Su, Z. Xu, G. Zhang, C. Shen, Q. Meng, Metal-organic framework channelled graphene composite membranes for H<sub>2</sub>/CO<sub>2</sub> separation, J. Mater. Chem. A 4 (2016) 18747–18752.
- [46] J.E. Gu, S. Lee, C.M. Stafford, J.S. Lee, W. Choi, B.Y. Kim, K.Y. Baek, E.P. Chan, J.Y. Chung, J. Bang, J.H. Lee, Molecular layer-by-layer assembled thin-film composite membranes for water desalination, Adv. Mater. 25 (2013) 4778–4782.
- [47] T. Kamada, T. Ohara, T. Shintani, T. Tsuru, Controlled surface morphology of polyamide membranes via the addition of co-solvent for improved permeate flux, J. Membr. Sci. 467 (2014) 303–312.
- [48] S. Kim, X. Lin, R. Ou, H. Liu, X. Zhang, G.P. Simon, C.D. Eastonc, H. Wang, Highly crosslinked, chlorine tolerant polymer network entwined graphene oxide membrane for water desalination, J. Mater. Chem. A 5 (2017) 1533–1540.
- [49] J. Wu, Z. Wang, Y. Wang, W. Yan, J. Wang, S. Wang, Polyvinylamine-grafted polyamide reverse osmosis membrane with improved antifouling property, J. Membr. Sci. 495 (2015) 1–13.
- [50] S. Karan, Z. Jiang, A.G. Livingston, Sub–10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation, Science 348 (2015) 1347–1351.
- [51] R.R. Nair, H.A. Wu, P.N. Jayaram, I.V. Grigorieva, A.K. Geim, Unimpeded permeation of water through helium-leak-tight graphene-based membranes, Science 335 (2012) 442–444.
- [52] K. Huang, G. Liu, J. Shen, Z. Chu, H. Zhou, X. Gu, W. Jin, N. Xu, High-efficiency water-transport channels using the synergistic effect of a hydrophilic polymer and graphene oxide laminates, Adv. Funct. Mater. 25 (2015) 5809–5815.
- [53] J.R. Werber, A. Deshmukh, M. Elimelech, The critical need for increased selectivity, not increased water permeability, for desalination membranes, Environ. Sci. Technol. Lett. 3 (2016) 112–120.
- [54] B. Shi, P. Marchetti, D. Peshev, S. Zhang, A.G. Livingston, Will ultra-high permeance membranes lead to ultra-efficient processes? Challenges for molecular separations in liquid systems, J. Membr. Sci. 525 (2017) 35–47.
- [55] W. Choi, J. Choi, J. Bang, J.H. Lee, Layer-by-layer assembly of graphene oxide nanosheets on polyamide membranes for durable reverse-osmosis applications, ACS Appl. Mater. Interfaces 5 (2013) 12510–12519.
- [56] G.D. Kang, C.J. Gao, W.D. Chen, X.M. Jie, Y.M. Cao, Q. Yuan, Study on hypochlorite degradation of aromatic polyamide reverse osmosis membrane, J. Membr. Sci. 300 (2007) 165–171.