CONSTRUCTION AND PERFORMANCE OF LAMINATED GRAPHENE OXIDE MEMBRANES FOR HIGH-SALINITY WATER DESALINATION BY THERMALLY DRIVEN PERVAPORATION

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ABSTRACT

Thermally driven pervaporation process exhibits great promise in desalination application due to its characteristics of combining low-grade heat with high selective membranes to attain efficient separation. The membrane with high and stable water permeation is of key importance in efficient utilization of thermal energy. In this work, high performance laminated graphene oxide (GO) membranes were prepared via pressure assisted filtration for desalination and waste water treatment by pervaporation. The interlayer spacing that affects the permeation and selectivity of GO membrane were tuned by inserting and crosslinking PVA in the GO lamination layers. The cross-linked GO-PVA membranes displayed an outstanding and stable water flux of 98.1 kg/m^2·h, high rejection over 99.9% and high thermal efficiency of 98% in desalinating 10 wt% NaCl solution at 85 °C. Moreover, the cross-linked membrane also exhibited intriguing separation performance in the treatment of organic-contaminated wastewater.

Keywords: pervaporation, desalination, laminated graphene oxide membrane, water flux, thermal efficiency

NONMENCLATURE

Abbreviations	
GO	Graphene oxide
PVA	Polyvinyl alcohol
GA	Glutaraldehyde
PV	Pervaporation

1. INTRODUCTION

Desalination by pervaporation (PV) is burgeoning rapidly due to its outstanding capability in handling high-salinity water [1, 2]. The permeate flux of most existing membranes like polymer or zeolite are not enough to satisfy the requirement of practical application. Currently, some innovative membranes fabricated by two-dimension (2D) nanomaterials demonstrates outstanding water flux in PV desalination due to unique mass transfer channels where water vapor molecules can unimpededly transport through, making GO membranes generate headlines in desalination [3]. Much effort has been devoted into adjusting the interlayer spacing of GO membranes. However, till now, a steadily and efficient way of tailoring any desired interlayer spacing of GO membranes for more effective sieving is still lacking. GO membranes are readily disintegrated in aqueous environment because of the high hydrophilicity of GO sheets. Covalent cross-linking is an effective way to reinforce the stability owing to the formation of sturdy covalent bonds. However, there seems to be a competition between stability and flux because of the consumption of hydrophilic groups after cross-linking process. Extra introducing hydrophilic groups is an effective way of offsetting the loss of hydrophilicity, and thereby maintaining high water flux.

Herein, a feasible strategy for concurrently enhancing water permeability and stability, and meanwhile effectively tuning interlayer spacing was designed by intercalating GO membranes with PVA. The stability of GO membranes were further reinforced by covalent cross-linking with glutaraldehyde. The effects
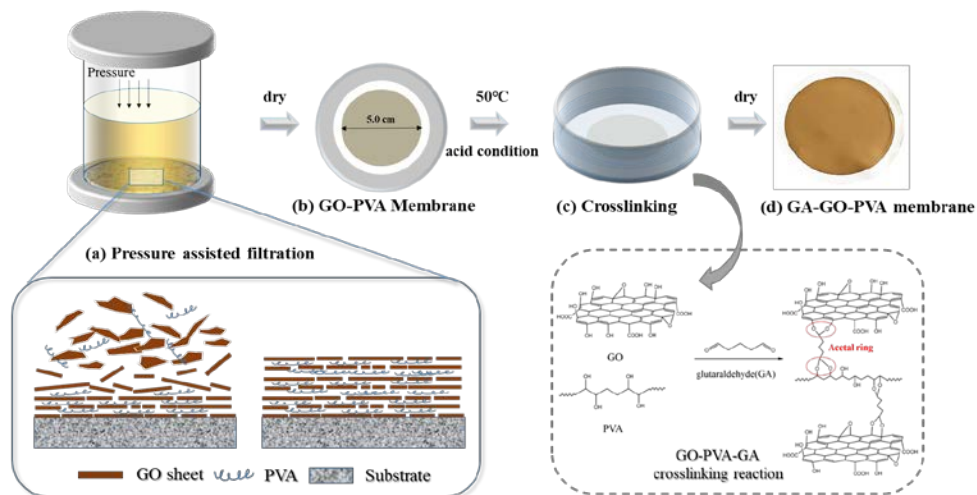
Fig 1 Illustration of the fabrication process of the GO composite membranes. (a) pressure-assisted filtration device and the schematic diagram of the construction of skeleton in GO-PVA active layer, (b) GO-PVA membranes, (c) cross-linking reaction of GA and GO-PVA membranes and (d) GA-GO-PVA membranes.

of GO deposition amount, PVA content and operation conditions on physicochemical structure, surface hydrophilicity and desalination performance were investigated. The resultant cross-linked GO membranes exhibit remarkable water productivity, satisfying produced water purity and robust structure even in handling organic-contaminated high-salinity wastewater.

2. EXPERIMENTAL

2.1 Materials

GO was synthesized from graphite with the modified Hummers method. The chemicals including PVA (Mw= 74800 g/mol, hydrolysis degree 97%), sodium chloride (NaCl), glutaraldehyde (GA, 75%), hydrochloric acid (HCl, 37 wt%) are all commercial products and used without further purification. And a commercial mixed cellulose ester (MCE) microfiltration membrane (pore size 0.22 μm) is chosen as the substrate for preparation of GO-PVA membranes.

2.2 Fabrication of GO-PVA membranes

The resulted GO was dispersed into DI water and sonicated for 4 h to obtain a 0.5 g/L stable aqueous GO suspension. A 0.5 g/L homogeneous PVA aqueous solution was prepared by dissolving PVA in DI water under stirring at 90°C for 4 h. The casting solutions were made by mixing 2 mL of the GO suspension and a certain volume (0 to 40 mL in this case) of the PVA solution and then diluting with DI water to total volume of 200 mL.
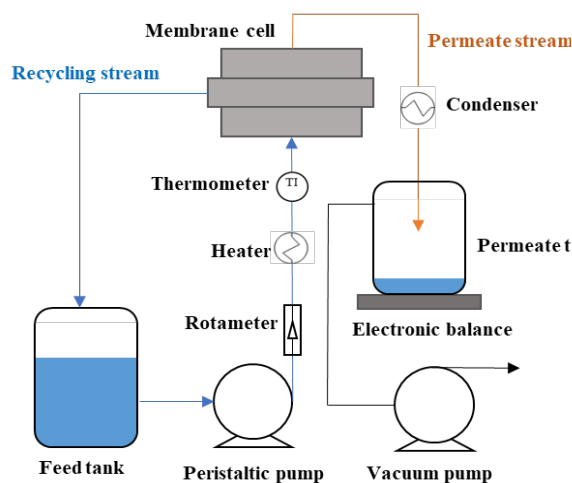

Fig 2 Schematic diagram of the lab-scale pervaporation desalination apparatus.

The laminated GO-PVA membranes were fabricated via the pressure-assisted filtration method (Fig 1a). The as-prepared membrane was dried in an oven at 50°C for 4 h (Fig. 1b). For the preparation of cross-linked membranes, the resultant GO-PVA membrane was firstly soaked in 200 mL DI water for 12 h at room temperature, and then added 1 mL GA and 2 mL HCl, heated the membrane at 50°C for 4 h (Fig. 1c). The membranes were marked as GO-PVA or GA-GO-PVA (x/y) according to whether cross-linked, where the x and y represent the volume of GO suspension and PVA solution in the casting solution, respectively.

2.3 Stability tests and PV desalination performance

The stability performance of GO-PVA membranes was evaluated by ultrasonic experiments.

The pervaporation tests were carried out by a lab-scale apparatus (Fig 2). The desalination performance was evaluated in terms of water flux (J) and salt rejection (R).

$$J = \frac{M}{A \times t}$$
(1)

where M (kg) is the weight variation of the feed, A is the effective membrane area (19.63 cm^2) and t (h) is the operation time.

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

where C_f and C_p represent the salt concentration in feed and permeate side, respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of membranes

The surface morphology of GO-PVA membranes with different PVA contents were characterized with SEM (Fig 3a–c) and AFM (Fig 3d–f). The GO layer completely covered the substrate and there are no defects or pores can be seen in the surface of membranes. The typical wrinkles of GO membranes become broader as the PVA content increases with the intercalation of PVA molecules into GO sheets. The roughness of GO-PVA membranes gradually increased from 48.1 to 62.3 nm. The increase in roughness of such hydrophilic material is considered to be beneficial to the surface hydrophilicity, and therefore to the water flux in PV desalination process.

Fig 4 shows the FTIR spectra of substrate, GO, GO-PVA and GA-GO-PVA membranes. Compared with pristine GO membrane, the progressively intensified peaks of GO-PVA membranes at 2920 cm^{-1} related to the stretching vibration of –CH$_2$ which only exists in PVA chains indicates the gradual increase of PVA amount. The peak at 2863 cm^{-1} derived from the stretching vibration of –CH groups of the GA molecules and the peak at about 1100 cm-1 corresponded to the C-O-C stretching vibration of acetal ring. As confirmed by FT-IR results, the PVA chains and GA molecules were introduced into GO layers and GO and PVA were successfully cross-linked by GA.

Fig 5a shows the XRD spectra of GO-PVA membranes, as PVA content increased, the diffraction peak of GO-PVA membranes shift leftwards from 11.21° to 6.76° progressively, corresponding to the interlayer spacing increasing from 0.79 to 1.31 nm (Fig 5b). The interlayer spacing of GO membranes were effectively tuned by the intercalation of flexible PVA chains. In
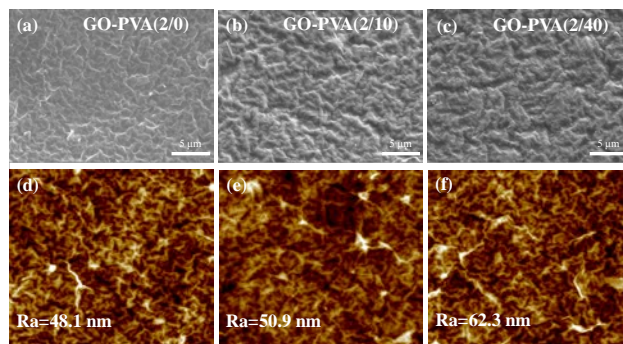

Fig 3 SEM (a-c) and AFM images (d-f) of GO-PVA membranes with different PVA content.
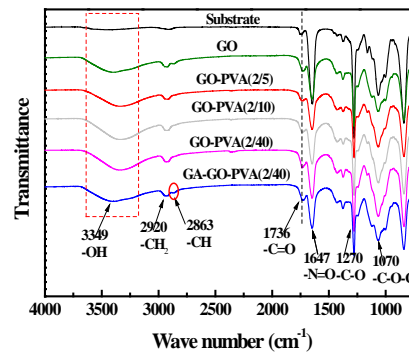

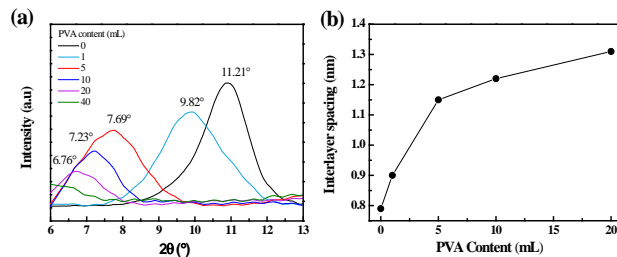Fig 4 FTIR spectra of the substrate, GO, GO-PVA and GA-GO-PVA membranes.

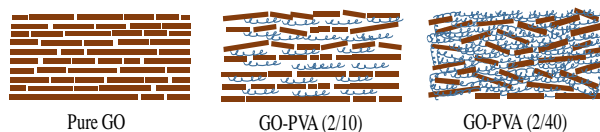Fig 5 XRD patterns (a) and interlayer spacing values (b) of GO-PVA membranes.

Fig 6 Brick-mortar model of GO-PVA composite structure.

addition, as PVA content increases, a gradually decrease on height and sharpness of the diffraction peaks was observed from the XRD patterns, suggesting that the orientation order of GO layer was decreased.

This interesting phenomenon is related to the variation of microstructure of the GO membranes when being intercalated by different contents of PVA. As illustrated by a brick-mortar model in Fig 6, the GO sheets were served as the bricks and the PVA molecular chains as the mortar. The pristine GO layer originally
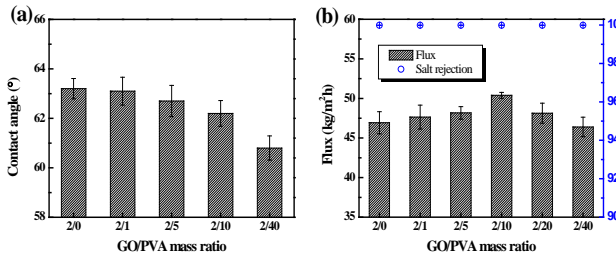
Fig 7 Effects of PVA content on (a) contact angles and PV desalination performance (65℃, 10 wt% NaCl).

exhibited a well-stacked laminated structure because of its inherent 2D shape and pressure-assisted filtration during fabrication. For GO-PVA membranes, the intercalation of PVA chains into the narrow space between GO sheets effectively enlarges the interlayer spacing of the membrane, and a widened mass transfer paths for water molecules was therefore built. Meanwhile, the laminated structure of the membrane is still basically kept.

The intercalation of PVA increasingly improves the membrane hydrophilicity (Fig 7a) besides widening its mass transfer channels. As for the desalination performance of GO-PVA membranes, the water flux firstly increased and then decreased as the PVA content increases (Fig 7b). So, it is unsuitable to add huge amount of PVA in terms of water flux. It is deduced that the ordered laminated structure, which constructed the nanochannels for water transport, is deconstructed by excessive addition of PVA. Obviously, there existed a contradiction between the ordered structure and the width of the nanochannels. On the one hand, the PVA enlarges the interlayer spacing, which favors the water flux, on the other hand, inserting extra PVA impact the regularity of GO laminar structure and increase the mass transfer resistance for water permeation.

3.2   Stability test and desalination performance

Ultrasonic experiments were carried out to exam the stability performance of the fabricated membranes. As shown in Fig 8a, some defects appeared on the surface of pristine GO membrane in 1-minute ultrasonic treatment, and after 5 minute, most of the GO layer peeled off from the support. The GO-PVA (2/10) membrane displayed a better endurance under ultrasonic testament (Fig 8b), the GO layer started to peel off after 10-minute ultrasonic treatment (Fig 7b). In the case of GA cross-linked membranes, the GA-GO-PVA (2/10) membrane (Fig 8c) can keep intact throughout the 10-minute ultrasound test and can eventually
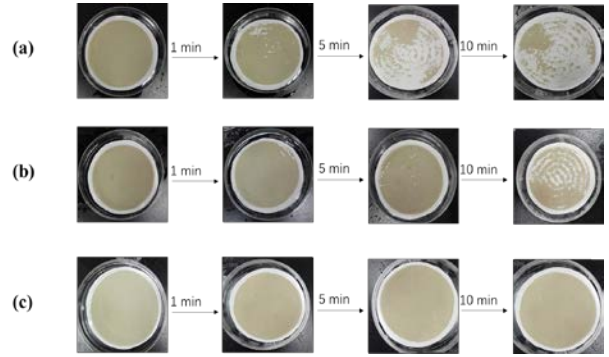

Fig 8 Stability of GO membranes under ultrasonic treatment: (a) Pure GO membrane (GO-2); (b) GO-PVA membrane (GO-PVA 2/10); (c) Cross-linked GO-PVA membrane (GA-GO-PVA 2/10).

withstand ultrasonic treatment over 70 minutes, demonstrating an excellent structural stability. The enhanced stability can be mainly ascribed to the combination effect of inserted PVA polymer chains and GA cross-linking. The intercalated flexible PVA chains can act as adhesive to connect the GO sheets via hydrogen bonds. Meanwhile, covalent cross-linking were carried out between GO, PVA and the substrate, which plays an important role in improving stability of the laminar GO membranes.
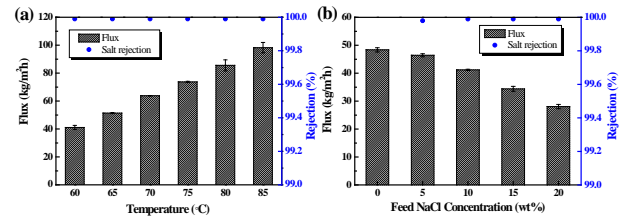

Fig 9 PV desalination performance: effect of   (a) feed temperature and (b) NaCl concentration.

As for the PV desalination performance of GA-GO-PVA (2/10) membrane, the water flux was gradually increased as feed temperature increased (Fig. 8a). The highest flux is 98.1 kg m^{-2} h^{-1} at the feed temperature of 85℃ for treating 10 wt% NaCl solution. And the salt rejection is as high as over 99.9%. As feed concentration increases, the water flux decreases (Fig 9b). The water flux is 28.3 kg m^{-2} h^{-1} for treating 20 wt% NaCl solution with 99.9% of salt rejection at 65℃, which is still at high level in treating with high-salinity water.

Materials	d_p (μm)	d-spacing (Å)	T (°C)	c_F (wt%)	J (kg/m^2·h)	R (%)
pPDA cross-linked GO/Al$_2$O$_3$[4]	1.0	11.29	90	3.5	10.7	99.8
PDI cross-linked GO/Al$_2$O$_3$[5]	1.0	10.59	90	3.5	11.4	99.9
CDA cross-linked GO/Al$_2$O$_3$[4]	1.0	9.09	90	3.5	20.1	99.9
GO/Al$_2$O$_3$[6]	–	~8.51	90	3.5	48.4	99.7
GO/PAN[7]	–	–	90	3.5	65.1	99.8
GO-PVA-GA/PAN[8]	0.22	–	70	3.5	69.1	99.9
GA-GO-PVA (2/10) (this study)	~0.5	1.22	85	10	98.1	> 99.98

d_p: pore diameter of support membrane; T: operating temperature; c_F: feed concertation.
pPDA: p-phenylenediamine; PDI: 1, 4-phenylene diisocyanate; CDA: 1, 4-cyclohyxanediamine; PAN: polyacrylonitrile; PVA: poly(vinylalcohol); GA: glutaraldehyde.
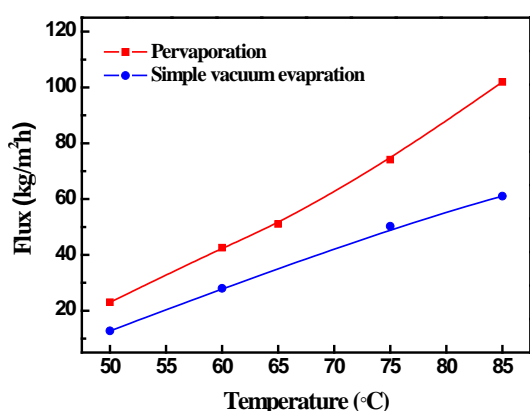

Fig 10 Comparison of water flux in (a) PV process and (b) simple vacuum evaporation process at different operating temperatures.

Table 1 compares the PV desalination performance of GA-GO-PVA (2/10) membrane with other GO membranes reported in the literature. The ultrahigh water flux and salt rejection even in treating high-salinity water demonstrate the superiority of the GO membranes prepared in this study.

The water productivity of PV process employing GO membrane was compared with simple vacuum evaporation without membrane (Fig 10). The water fluxes in PV process is much higher than vacuum evaporation, especially at 85°C, 1.68 times increment was achieved. The highly hydrophilic membrane surface favors the water capture into the membrane, which ensures the rapid dissolution of water in membrane on the basis of solution-diffusion model. Additionally, a large capillary pressure can be generated as a result of the extremely narrow width of channels and interphase existing in PV process, which can draw water molecules from the feed side to the phase interface swiftly, thus guarantee the fast diffusion inside the membrane. Correspondingly, the high water flux means high efficiency of thermal energy utilization in the water permeation and evaporation process through the membrane. The thermal efficiency of PV process was as high as 98% by calculation according to water vapor latent transported through membrane, which is much larger than that of simple vacuum evaporation process. This result indicates that the vast majority of energy was effectively devoted into the production of water, demonstrating its promising prospect in high-efficiency desalination.

4. CONCLUSIONS

In conclusion, a highly-stable GA-GO-PVA membranes were fabricated via pressure-assisted filtration and cross-linking methods. The membranes were characterized in details by various characterization methods. By using PVA as intercalation molecule, the adhesion strength was increased as well as the interlayer spacing. The stability and water flux of GO membranes were enhanced synchronously. The cross-linked GA-GO-PVA membranes has shown impressive desalination performance with high water flux (98.1 kg m^{-2} h^{-1}, 85°C, 10 wt% NaCl) , high salt rejection (over 99.9%) and high thermal efficiency (98%) in treating high-salinity water.

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