1	Polyvinylpyrrolidone modified graphene oxide as a modifier for thin film composit			
2		forward osmosis membranes		
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# 12 Abstract

13 Polyvinylpyrrolidone (PVP) modified graphene oxide (GO), hereinafter referred to 14 as PVP-GO, was synthesized as a novel modifier to fabricate thin film nanocomposite 15 forward osmosis membranes. The results indicated that by coating PVP on the surface of 16 GO nanosheets, the dispersibility of GO was increased and the aggregation of GO was 17 reduced. Compared with the pristine and GO modified FO membranes, the PVP-GO 18 modified membranes enhanced the desalination performance giving both a higher water 19 flux and lower reverse solute flux. When using 2 mol  $L^{-1}$  of NaCl as the draw solution and 10 mmol $\cdot$ L<sup>-1</sup> NaCl as the feed solution, the water flux of the FO membrane modified 20 with 0.0175 wt.% of PVP-GO reached 33.2 LMH in the ALDS mode (the active laver 21 22 facing the draw solution), which was 3.3 times higher compared with the water flux of 23 the pristine FO membranes. Improved desalination performances of PVP-GO modified 24 FO membranes were attributed to the better dispersibility of the PVP-GO nanosheets and 25 increased surface hydrophilicity of the modified FO membranes. This study indicated that 26 PVP-GO is an effective modifier to enhance the performance of FO membranes.

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Keywords: Graphene oxide; Forward osmosis; Thin film nanocomposite membrane;
 Desalination

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## 1 **1. Introduction**

2 Membrane-based techniques such as ultrafiltration (UF), nanofiltration (NF), and 3 reverse osmosis (RO) are commonly applied to manage waste water treatment and 4 seawater desalination [1-3]. Forward osmosis (FO) is a process that uses an osmotic 5 pressure gradient as the driving force to extract pure water out of saline water. In the 6 water treatment area FO has been seen as having potential due to prospective lower 7 energy costs and positive effects with regard to the mitigation of membrane fouling 8 compared to traditional pressure-driven membranes [4-8] but reservations about its 9 industrial potential have been expressed [9]. The challenges include the need for thin film 10 composite FO membranes (TFC-FO) to have higher water fluxes, reduced reverse flux of 11 salt and the need to lessen internal concentration polarization (ICP) [10-12].

12 Many studies have been performed to improve TFC membrane performance through 13 membrane modifications. One of the most prevalent strategies is to embed nanoparticles 14 into membranes. It was reported that materials such as silver, TiO<sub>2</sub>, carbon nanotubes 15 (CNTs), and ZnO could be blended into membranes to alter certain membrane properties including porosity, roughness and hydrophilicity, which enhanced membrane 16 17 performances [13-16]. Another strategy is to modify the surface of the membranes either 18 to improve membrane permeability/rejection or to reduce fouling. It was reported that by 19 adding silicon dioxide into aqueous solutions during the interfacial polymerization 20 process, the water flux of the FO membrane was increased and the reverse solute flux 21 was reduced [17]. Embedded silver nanoparticles into the surface of membranes has been 22 found to reduce the membrane fouling since silver nanoparticles interacted with bacteria 23 directly [18-21].

Recently carbon-based nanomaterials have attracted attention as a novel membrane modifier. Among these nanomaterials, graphene and graphene oxide (GO) have become buzzwords in recent years due to advantages such as large surface area, great compatibility, prominent electron transport and great mechanical properties [22]. Enhancements of both water flux and sodium sulfate rejection were reported when GO was added into polysulfone (PSf) ultrafiltration (UF) membranes [23]. Ionita and coworkers found that GO modified PSf-UF membranes showed improved thermal and

1 mechanical performances [24]. However, the required added amount of nanoparticles was 2 rather large with over 0.25 wt.% [24]. Previous reports associated with RO membrane 3 modification have focused on adding a relatively small amount of GO directly into the 4 aqueous phase solution during the interfacial polymerization process. Whilst there were 5 observed improvements in membrane performances such as water flux, salt rejection and antifouling, the aggregation of GO could not be ignored at a relatively high concentration 6 7 [25, 26]. Ali and co-workers reported that the separation performance of TFC membranes 8 was reduced when the concentration of GO was higher than 0.015 wt.% of aqueous phase 9 solution [27]. Therefore, it is important to have a more efficient strategy for proper 10 dispersion of graphenes and grahene oxide.

11 Polyvinylpyrrolidone (PVP), a pore-forming macromolecule with non-ionic and non-12 toxic properties, is a common reagent to control the microstructure of UF membranes [28], it 13 is also a hydrophilic modifier to reduce membrane fouling [29]. Moreover, previous studies have confirmed that PVP is an excellent surface modifier in improving and 14 15 stabilizing the dispersion of nanoparticles [30]. It was reported that graphenes could be 16 detached from graphites by using PVP in the aqueous phase under sonication, which 17 enabled polymer-coated single layers of graphenes to disperse stably in the aqueous phase 18 [31]. Besides these advantages, however, PVP is easily washed away and difficult to retain 19 inside membranes [32]. An appropriate solution should be provided to reduce the run off 20 of PVP if using it for membrane surface modification.

21 To this end, a novel material, PVP-GO was prepared by coating PVP with graphene 22 oxide nanoparticles (PVP-GO), which could not only increase the dispersion of GO but 23 also reduce the run off of PVP at the same time. In addition, the feasibility of PVP-GO as 24 a membrane modifier was investigated. PVP-GO modified FO membranes were 25 characterized and their desalination performance investigated and compared with that of 26 GO modified FO membranes. Moreover, the optimal loading of PVP-GO on the FO 27 membranes was also investigated in this work. To the best of our knowledge, this is the 28 first time that the feasibility of PVP-GO to modify the surface of FO membranes has 29 been investigated.

## 30 2. Experimental

#### 1 2.1. Materials

2 Polysulfone (PSf, Solvay P3500) was purchased from BASF Co., Ltd. (China). 1methyl-2-pyrrolidinone (NMP,  $\geq$  99%) was bought from Sinopharm Chemical Reagent 3 4 Co., Ltd. (China). Trimesoyl chloride (TMC, 98%) and m-phenylenediamine (MPD) 5 were purchased from Aladdin (China). n-hexane (99%, Sinopharm Chemical Reagent Co., 6 Ltd., China) was applied as the solvent of TMC. Graphene oxide (GO) (Aladdin, China) 7 contains 30-40% oxygen-containing functional groups and a few layers of graphene 8 oxide, in a thickness ranging from 0.55 to 1.2 nm. The TEM image of graphene oxide is 9 shown in Fig. S1 in the Supporting Information. Polyvinylpyrrohdone (PVP K30, Sigma-10 Aldrich, China) and L-ascorbic acid (L-AA, 99%, Alfa Aesar, China) were used for 11 graphene oxide modification. In addition, sodium chloride (NaCl) from Sinopharm 12 Chemical Reagent Co., Ltd. (China) was used for membrane performance testing.

#### 13 2.2. Preparation of PVP-GO nanoparticles

14 The PVP-GO was prepared by a synthesis method given in previous reports [25, 33]. 15 Fig. 1 shows the schematic diagram of PVP-GO preparation. In this experiment, 250 mg 16 of GO was added into 100 ml of deionized water and sonicated for 30 min to achieve the 17 uniform dispersion. Following that, 25 mg of PVP and 50 mg of L-AA were added into 18 the homogeneous GO dispersion at the same time. Initially the mixture was stirred for 10 19 min at room temperature and then for 4 h in a 80 °C water bath. Later, the suspension 20 was centrifuged at 12,000 rpm for 15 min and washed with deionized water to remove 21 excess PVP and L-AA. Finally, the product was re-dispersed into 100 ml deionized water for future use. For comparison, the homogeneous 25 mg·L<sup>-1</sup>GO dispersion was stirred 22 23 under room temperature for 4 h and 10 min without the addition of PVP and L-AA. 24 Similarly, the GO dispersion was centrifuged and re-dispersed into 100 ml deionized 25 water.

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## 4 2.3. Preparation of GO and PVP-GO modified FO membranes

The PSf substrate membrane was prepared through a typical phase inversion
technique. Generally, 0.5 wt.% of PVP and 17.5 wt.% of PSf were dissolved into 82 wt.%
NMP. The casting solution was spread on a clean glass plate at a knife height of 175 μm.
The permeate flux of pure water of this substrate membrane was approximately 367
LMH under a pressure of 0.1 MPa, tested by a dead-end filtration testing system.
Moreover, the rejection of 1 g·L<sup>-1</sup> of bovine serum albumin (BSA) was 99.4%.

The prepared GO and the PVP-GO solution were diluted into the specific concentrations listed in Table 1. After that, 2.0 wt.% MPD was added into solutions containing different amounts of GO and PVP-GO, respectively. Through interfacial polymerization, the dense active polyamide (PA) layer of the FO membrane was prepared on the substrate membrane. Firstly, 2.0 wt.% MPD aqueous solution containing nanoparticles were poured onto the surface of the substrate membrane for 2 min. Excess MPD aqueous solution was removed by a rubber roller. After that, 0.1 wt.% TMC dissolved in n-hexane was poured onto the surface of the membrane. After 1 min, the
TMC solution was drained off. Later, the membrane was stored in an oven under 60 °C
for 8 min. Finally, the membrane was stored in a deionized water bath for future use.
According to the amount of GO in MPD solution, the membranes were named as GOFO-1, GO-FO-2, GO-FO-3, GO-FO-4, GO-FO-5 and GO-FO-6, while PVP-GO modified
FO membranes were labeled as PGO-FO-1, PGO-FO-2, PGO-FO-3, PGO-FO-4, PGOFO-5 and PGO-FO-6.

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9 **Table 1.** The concentration of nanoparticles in MPD solutions for interfacial polymerization.

Membrane	GO (wt.%)	Membrane	PVP-GO (wt.%)
TFC-FO	0		
GO-FO-1	0.0075	PGO-FO-1	0.0075
GO-FO-2	0.0100	PGO-FO-2	0.0100
GO-FO-3	0.0125	PGO-FO-3	0.0125
GO-FO-4	0.0150	PGO-FO-4	0.0150
GO-FO-5	0.0175	PGO-FO-5	0.0175
GO-FO-6	0.0200	PGO-FO-6	0.0200

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11 2.4. Characterization of GO and PVP-GO nanoparticles

12 Ultraviolet-visible (UV-vis) spectra of GO and PVP-GO solutions were measured 13 using a Cary-50 UV-vis spectrometer (Varian, USA). Attenuated total reflectance-14 infrared spectroscopy (ATR-FTIR, Nicolet iS10, Thermo Fisher Scientific, USA) was 15 used to estimate the functional groups of nanoparticles. Additionally, Raman scattering 16 spectra of GO and PVP-GO were collected by a LabRAM Aramis (HORIBA JobinYvon) 17 confocal micro-Raman system. For obtaining Raman spectra, one drop of GO and PVP-18 GO solution was placed onto clean silicon wafers as the SERS substrate, respectively. 19 After drying under room temperature, the Raman signals of GO and PVP-GO molecules 20 were detected. Zeta potential of GO and PVP-GO solution were analysed by a ZetaPALS 21 Zeta Potential Analyzer.

## 22 2.5. Characterization of FO membranes

1 In order to estimate the functional groups in the membrane surface, infrared spectra 2 of membranes were obtained by ATR-FTIR. Before investigation, membrane samples 3 were kept at room temperature for 24 h to dry. Additionally, in order to investigate the hydrophilicity of membranes, a sessile drop analysis system (DSA100, KRUSS, 4 5 Germany) was applied to measure the contact angle of the membranes. The contact angles were tested immediately after placing a drop of deionized water on the surface of 6 7 membranes. Prior to testing, every membrane sample was dried at room temperature for 8 24 h. Additionally, a field emission scanning electron microscope (FESEM, HITACHI S-9 4800, Japan) system was in place to observe the surface morphology of FO membranes. 10 Before testing, all samples were kept in an oven for 48 h at 80 °C. Membrane surface 11 roughness was analyzed by atomic force microscopy (AFM) (Aglient, USA) used in a 12 peak force tapping mode in air.

#### 13 2.6. Evaluation of desalination performance of FO membranes

14 All membranes were tested in a forward osmosis test system, which has been 15 described previously [16, 34], in both the ALFS mode (the active layer facing the feed 16 solution) and the ALDS mode (the active layer facing the draw solution) under room temperature. The total active membrane area was  $33.8 \text{ cm}^2$ , the draw solutions were 2 17  $mol \cdot L^{-1}$  NaCl and 0.5  $mol \cdot L^{-1}$  NaCl solution, respectively, while 10  $mmol \cdot L^{-1}$  NaCl was 18 19 used as the feed solution. Both the draw solutions and the feed solutions were maintained at a cross-flow rate of 20 L·h<sup>-1</sup>. The weight change of the draw solutions and the 20 21 conductivity change of the feed solution were measured by a digital weight balance and a 22 conductivity meter, respectively. After 20 min of the FO system becoming stable, the 23 water flux  $(J_w)$  and the reverse solute flux  $(J_s)$  were recorded. Both  $J_w$  and  $J_s$  were examined every 15 min over 5 times to calculate the average value. The following 24 25 equations were applied for the calculation of water flux and reverse solute flux, 26 respectively.

$$J_w = \frac{\Delta V}{\Delta t \cdot A_m} \tag{1}$$

$$J_s = \frac{\Delta(C_t V_t)}{\Delta t \cdot A_m} \tag{2}$$

1 where  $\Delta V$  is the volume of permeated water (L),  $A_m$  is the membrane area (m<sup>2</sup>), and  $\Delta t$  is 2 the permeation time (h),  $C_t$  is the concentration of NaCl at the end of permeation time,  $V_t$ 3 is the volume of permeated water at the end of permeation time (L).

## 4 **3. Results and discussion**

## 5 3.1. Characterization of GO and PVP-GO nanosheets

6 Fig. 2a shows pictures of GO and PVP-GO aqueous dispersions immediately and 7 two weeks after being prepared. It was observed that there was no obvious precipitation 8 of either GO or PVP-GO. Fig. 2b illustrates the UV-vis spectra result of GO, PVP and 9 PVP-GO. Some typical peaks could be observed in GO nanosheets. The peak at 230 nm 10 is associated with the  $\pi$ - $\pi$ \* transitions caused by the C-C bonds of the aromatic skeleton, while a shoulder peak at 300 nm resulted from the  $\pi$ - $\pi$ \* transitions caused by the C-O 11 12 bonds of carboxylic acid [25, 33, 35]. Compared with GO, PVP-GO showed an obvious 13 peak at 197 nm which is the typical peak of PVP, indicating that PVP was successfully coated on the surface of GO. Another difference between the spectra of PVP-GO and GO 14 15 was that the absorption peak which was at 230 nm in GO shifted to at 270 nm in PVP-GO, while the intensity of the shoulder peak at 300 nm decreased, which showed that GO was 16 17 reduced [35, 36]. In addition, the reduction of GO was the reason for color differences 18 between GO and PVP-GO aqueous dispersions.



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**Fig. 2.** (a) Photographs of aqueous dispersions of GO and PVP-GO taken immediately after preparation and two weeks later, (b) UV-vis spectra of aqueous dispersions of PVP, GO and PVP-GO.

6 Fig. 3a shows the ATR-FTIR spectra of GO and PVP-GO. It could be observed that there was a peak at 1726 cm<sup>-1</sup> in the spectra of GO due to the oxygen-containing groups 7 8 on the surface of the GO [37]. Nevertheless, the peak disappeared in the spectra of PVP-9 GO, indicating that some oxygen-containing groups on the GO surface were removed, 10 and certain chemical bonds were built up between PVP molecules and some functional 11 groups on the surface of GO sheets [37]. This change of PVP-GO indicated that GO was 12 reduced by L-AA during the process of PVP-GO preparation. It was reported that at the 13 beginning stage of PVP-GO synthesis, some tert-amide groups in PVP are protonated 14 because of L-AA. After that, these active *tert*-amide groups reacted with the epoxide or 15 the hydroxyl groups surrounding the surface of GO before the functional groups were 16 reduced by L-AA (Fig. 1) [37]. The reduction of GO was also confirmed through evidence of Raman scattering (Fig. 3b). The spectra of GO indicated that there were two 17 characteristic peaks at 1338 cm<sup>-1</sup> and 1595 cm<sup>-1</sup>, which represented the D band and the G 18 19 band, respectively [38]. After the GO was coated with PVP, the intensity ratios of the D

and the G band of PVP-GO increased from 0.97 to 1.29, confirming that the GO was 1 reduced during the preparation of PVP-GO [39]. However, the peak at around 3443 cm<sup>-1</sup> 2 3 of the ATR-FTIR spectra of PVP-GO suggested that there were still hydroxyl groups on the surface of the PVP-GO [40]. The zeta potential (ZP) of GO and PVP-GO aqueous 4 5 solutions were tested. Zeta potential reflects how much charged particles repel each other 6 in dispersion. Thus, a high absolute value of zeta potential generally indicates that the 7 level of aggregation is low and the dispersion is stable [38, 41-43]. Results showed that the zeta potential was -25.0 mV for GO and -35.1 mV for PVP-GO, which revealed a 8 9 higher stability of PVP-GO aqueous solution than the GO aqueous solution.



Fig. 3. (a) ATR-FTIR spectra of GO and PVP-GO nanosheets, (b) Raman spectra of GO and
 PVP-GO nanosheets.

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#### 3.2. Characterization of FO membranes

15 ATR-FTIR spectra of the pristine TFC-FO membrane and membranes modified by 0.015 wt.% of GO (GO-FO-4) and PVP-GO (PGO-FO-4) were examined (Fig. 4). It was 16 17 observed that all FO membranes showed some typical peaks of polyamide membranes prepared by interfacial polymerization of MPD and TMC. The peaks at 1322, 1295 and 18 1146 cm<sup>-1</sup> were due to the stretching vibration of the asymmetric sulfur dioxide while the 19 20 peak at 1411 cm<sup>-1</sup> was attributed to C-H symmetric deformation vibration of  $-C(CH_3)_2$ [44]. Evidence of the existence of GO and PVP-GO on the surface of modified TFC-FO 21 membranes was shown in a new broad peak around 3443 cm<sup>-1</sup>, which belonged to the 22 hydroxyl stretching vibration of GO and PVP-GO [40]. Due to the small amount of 23 24 nanoparticles, this peak was not obvious. Compared with the pristine TFC-FO

membranes, GO and PVP-GO modified membranes showed increasing transmittance intensity at 1726 cm<sup>-1</sup>. This is due to the oxygen-containing groups on the GO and PVP-GO surface which is in line with the results of ATR-FTIR measurements on GO and PVP-GO. These results together confirmed the presence of GO and PVP-GO nanosheets on the surfaces of FO membranes after interfacial polymerization.



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Fig. 4. ATR-FTIR spectra of TFC-FO, GO-FO-4 and PGO-FO-4 membranes.

9 Fig. 5 shows the water contact angles of FO membranes modified by different 10 amounts of GO or PVP-GO. It was observed that the contact angles decreased with the 11 increasing concentrations of GO or PVP-GO. This was due to the hydroxyl functional 12 groups around GO and PVP-GO, which were confirmed by the ATR-FTIR results shown 13 in Fig. 3a and Fig. 4, respectively. Moreover, compared with the contact angles of GO-14 FO membranes, PGO-FO membranes showed slightly lower contact angles at the same 15 concentration of nanoparticles. This indicated that the hydrophilic PVP also increases the hydrophilicity of membrane surface, which was in line with other research [32]. 16

Therefore, it could be expected that PVP-GO modified FO membranes might
 demonstrate a higher water flux.



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Fig. 5. Contact angles of membranes with different concentrations of GO and PVP-GO.

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6 Fig. 6 shows the FESEM images of the surface of thin film nanocomposite forward 7 osmosis (TFN-FO) membranes and of a TFC-FO membrane. The typical "ridge and 8 valley" structures formed by the interfacial polymerization process were found in all 9 membranes [45]. It could be observed that the pristine TFC-FO membrane had a dense 10 cross-linking network that covered the globular structure and left only a few globules 11 exposed. While GO concentrations increased, more globules were observed on the 12 surface of membranes (Fig. 6b and 6d). There were some regions on the GO-FO-6 13 membrane that were smooth and without any cover of globules or crosslinking networks. 14 A computer software "Image J" was used to measure the percentage of smooth area on 15 the membrane surfaces. Firstly, the area of smooth regions (in Fig. 6d and Fig. 6e 16 respectively) were highlighted and measured by the software. After that, the area of the

1 smooth regions was divided by the total area of the SEM image to illustrate the 2 percentage of smooth area on membrane surfaces. Results indicated that the smooth area of GO-FO-6 occupied almost 37.9% of the membrane surface in Fig. 6d, while PGO-FO-3 4 6 had a smooth area of 17.3%. The effect of GO and PVP-GO on surface roughness was 5 also investigated by analyzing the surface topology using AFM. Fig. 7 shows the three dimensional AFM images of the top surface of the pristine TFC-FO, GO-FO-5, PGO-FO-6 7 5, GO-FO-6 and PGO-FO-6 membranes with a scan size of 5  $\mu$ m  $\times$  5  $\mu$ m. Table 2 shows 8 the average arithmetic roughness (Ra), root mean square roughness (Rq) and 9 irregularities (Rz) of these membranes. Compared with the pristine TFC-FO membrane, 10 GO modified FO membranes and PVP-GO modified FO membranes showed smoother 11 surfaces. Moreover, when FO membranes were modified by the same concentration of 12 nanosheets, PVP modified FO membranes showed less reduction of roughness 13 parameters than GO modified FO membranes. The reason for these smooth areas and the 14 reduction of roughness was connected to the interaction of aggregated GO during the 15 interfacial polymerization process. The formation of ridge structures depended on the 16 diffusion of MPD into the organic side during the interfacial polymerization process. 17 When GO nanosheets were embedded into the MPD solution, they would transversely 18 adhere to each other during the interfacial polymerization process. As a result, the 19 aggregation of GO nanosheets interfered with the diffusion of MPD and hindered the 20 development of the ridge structures [46-48]. Compared with GO modified FO 21 membranes, the reduced smooth area in PVP modified FO membranes was potentially 22 due to the better dispersibility of PVP-GO than GO, and a reduced amount of aggregation. 23 Fig. 8 exhibits the cross-sections of the TFC-FO membrane and PGO-FO-5. Using 24 "Image J", the thickness of the PA layer was measured by comparing the width of the PA 25 layer and the scale in SEM images. 20 locations were selected in each SEM image to 26 calculate the average thickness of the PA layer. It could be observed that the thickness of 27 the polyamide layer of PGO-FO-5 membrane was 154 nm, which was less than the 253 28 nm of the TFC-FO membranes. This result was in line with other research and was 29 potentially caused by the interference of GO with the interfacial polymerization process 30 which, as noted above, hindered the formation of ridge structures on the surface of TFC 31 membranes [46, 49].



Fig. 6. SEM images of surfaces of (a) TFC-FO, (b) GO-FO-5, (c) PGO-FO-5, (d) GO-FO-6, and
(e) PGO –FO-6 membranes.



Membrane	Ra (nm)	Rq (nm)	Rz (nm)	
TFC-FO	$19.9 \pm 2.0$	$24.8 \pm 2.7$	$124 \pm 5.0$	
GO-FO-5	$14.5 \pm 0.4$	$17.7\pm0.5$	$87.3\pm0.9$	
PGO-FO-5	$18.1 \pm 1.9$	$21.8 \pm 1.3$	$97.3 \pm 3.7$	
GO-FO-6	$11.9 \pm 0.3$	$14.8\pm0.6$	$70.6 \pm 3.3$	



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Fig. 8. SEM images of cross sections of (a) TFC-FO membrane, and (b) PGO-FO-5 membrane. *3.3. Desalination performances of FO membranes*

7 Fig. 9 and 10 show the water fluxes of the FO membranes modified by different 8 concentrations of GO and PVP-GO in the ALFS mode and the ALDS mode with 9 different concentrations of draw solutions. It could be observed that the water fluxes of 10 both GO-FO and PGO-FO membranes showed similar tendencies; with increasing 11 concentrations of modifers the water fluxes initially increased and reached optimal values 12 typically being at 0.015 wt.% for GO and 0.0175 wt.% for PVP-GO. Compared with the 13 TFC-FO membrane, all TFN-FO membranes showed enhancements in water fluxes, 14 which indicated both GO and PVP-GO were good modifiers to improve the water flux for FO membranes. The optimal water flux of GO-FO membranes was achieved when 0.015 15 16 wt.% of GO was added into the MPD solution, with the water flux increasing 62.2% (from 6.66 LMH to 10.80 LMH) in the ALFS mode and 58.4% (from 10.19 to 16.4 LMH) 17 in the ALDS mode when using 2 mol· $L^{-1}$  NaCl solution as the draw solution. Under the 18 same operating conditions, the PGO-FO-5 membrane showed the highest water flux 19 20 which increased 113% in the ALFS mode and 226% in the ALDS mode. This 21 enhancement of water fluxes was due to the improvement of the hydrophilicity 22 introduced by the hydrophilic functional groups around the surface of GO and PVP-GO.

The hydrophilic surface improved the adsorption of water molecules on the membrane surface and possibly increased the diffusion rate of water molecules passing through the modified membranes [44, 50]. Moreover, the thinner polyamide layer of the TFN-FO membranes was also was a critical factor in improving the water fluxes.

5 Compared with the water fluxes of GO-FO membranes, the water fluxes of all the PVP-GO modified membranes were higher when modified by the same concentration of 6 GO. This was potentially associated with enhancements in both the hydrophilicity and the 7 8 dispersibility of PVP-GO. It has been reported that PVP tends to attract water molecules 9 [37, 51] which would enhance the relative hydrophilicity of PVP-GO membranes. 10 However, when the concentration of GO and PVP-GO reached 0.0175 wt.% and 0.02 wt.%, respectively, the water fluxes had passed their optima. This could be due to 11 12 aggregation of nanoparticles at higher concentrations. As shown in SEM and AFM 13 images, an enlarged smooth area could be observed when the concentration of GO 14 increased to 0.02 wt.%, (Fig. 6d and 7d). The smooth region on the surface of the GO-15 FO-6 membrane reduced the surface roughness and resulted in a smaller active area of 16 the PA layer, consequently reducing the water flux. Compared with the GO-FO-6 17 membrane, the PGO-FO-6 membrane had fewer smooth regions. This is potentially due 18 to the PVP-GO being better dispersed.





Fig. 9. Water flux of FO membranes in the ALFS mode (a)  $0.5 \text{ mol} \cdot \text{L}^{-1}$  of draw solution, (b) 2.0 mol·L<sup>-1</sup> of draw solution. 10 mmol·L<sup>-1</sup> NaCl as the feed solution and cross-flow rate was 20 L·h<sup>-1</sup>.



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Fig. 10. Water flux of FO membranes in the ALDS mode (a) 0.5 mol·L<sup>-1</sup> of draw solution, (b) 2.0
mol·L<sup>-1</sup> of draw solution. 10 mmol·L<sup>-1</sup> NaCl as the feed solution.

5 The ratio of reverse solute flux and water flux is another critical factor with which to 6 evaluate the performance of FO membranes [52]. Higher ratios indicate that there is 7 relatively more salt moving from the draw solution to the feed solution and the membrane 8 has looser dynamic pore structure [53]. Fig. 11 shows the values of  $J_S/J_W$  of FO membranes modified by different amounts of GO and PVP-GO. Generally, the trend of 9 10 J<sub>S</sub>/J<sub>W</sub> for both the GO-FO and the PVP-GO-FO membranes reduced and then increased 11 along with increasing concentrations of nanosheets. Under all four operating conditions, 12 it could be observed that GO-FO-4 and GO-FO-5 showed the lowest values of J<sub>S</sub>/J<sub>W</sub>. 13 Compared with values of J<sub>S</sub>/J<sub>W</sub> of the GO-FO membranes, more obvious reductions could be observed on J<sub>S</sub>/J<sub>W</sub> of PGO-FO membranes. Specially, when the concentration of PVP-14 GO was 0.015 or 0.0175 wt.%, the J<sub>S</sub>/J<sub>W</sub> of PVP-GO-FO membrane was at a minimum. 15 16 Not unexpectedly the concentrations which maximised water flux also minimised  $J_S/J_W$ . 17 Thus when the concentration of GO was larger than 0.015 wt.% and when the 18 concentration of PVP-GO was larger than 0.0175 wt.%, the values of J<sub>S</sub>/J<sub>W</sub> of modified 19 membranes increased. This could be caused by the aggregation of nanoparticles.





Fig. 11. Ratio of reverse solute flux and water flux of modified FO membranes with different
amounts of GO and PVP-GO in (a) ALFS mode with 0.5 mol·L<sup>-1</sup> of draw solution, (b) ALFS
mode with 2.0 mol·L<sup>-1</sup> of draw solution, (c) ALDS mode with 0.5 mol·L<sup>-1</sup> of draw solution, and (d)
ALDS mode with 2.0 mol·L<sup>-1</sup> of draw solution. 10 mmol·L<sup>-1</sup> NaCl as the feed solution.

# 8 4. Conclusion

9 In this study, PVP coated GO was prepared and the effects of PVP-GO on the 10 desalination performances of TFN-FO membranes were investigated. Compared with GO 11 nanosheets, results for PVP-GO displayed better dispersion and a lower tendency of 12 aggregation. In addition, PVP-GO modified FO membranes exhibited excellent 13 desalination performance, including improved hydrophilicity, enhanced water flux and 14 reduced reverse solute flux compared to the pristine and GO modified FO membranes. 15 Moreover, the negative influences of the aggregation of nanoparticles on the performance 16 of membranes were reduced when PVP-GO was used in the replacement of the GO

modifier. The optimal loading of nanosheets on MPD was dependent on different types of
nanoparticles. Among all of the modified TFN-FO membranes, the membrane that was
modified with 0.0175 wt.% PVP-GO nanosheets showed the optimal desalination
performance.

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