Enhancing the Efficiency of a Forward Osmosis Membrane with a Polydopamine/Graphene Oxide Layer Prepared Via the Modified Molecular Layer-by-Layer Method

Chi-feng Lin, Li-han Chung, Guan-you Lin, Min-Chao Chang, Chi-Young Lee, and Nyan-Hwa Tai*

1. INTRODUCTION

The growing worldwide population has made clean water crisis increasingly serious. By 2025, two-thirds of the world’s population may face the water scarcity problem. This situation has prompted scientists to find a convenient energy-efficient method to purify water. In recent years, forward osmosis (FO) has attracted extensive attention due to its superior properties such as low energy input, high fouling resistance, and high water recovery.

With these distinctive advantages, the FO technology has been widely used in many applications, including desalination, power generation, wastewater treatment, food processing, and pharmaceutical industry. However, fabrication of the FO membrane still has some critical challenges. The primary drawback is the internal concentration polarization (ICP) effect during FO operation. The ICP effect results in inefficient mass transport in the membrane and reduces the net driving force across the membrane. The ICP effect can be minimized using a membrane with high porosity, low tortuosity, and minimized thickness to facilitate mass transfer. Typically, the FO membrane is a thin-film composite (TFC) membrane consisting of a microporous supporting layer that provides sufficient mechanical strength and an ultrathin polyamide (PA) active layer for selectivity.

In an attempt to optimize the FO performance of TFC membranes, researchers have altered the structure of substrates and incorporated nanomaterials such as carbon nanotubes (CNTs), titanium oxide (TiO2), and graphene oxide (GO) to improve the properties of the FO membrane. Apart from these solutions, dual-blade co-casting and electrospun nanofibers have been confirmed to be effective methods to increase the pore connectivity and porosity of the substrate. Among all of the techniques, GO-modified substrates offer a promising approach to promote the FO performance. This is because GO contains abundant functional groups such as carboxyl, hydroxyl, and epoxide groups, which are able to improve both the physical and chemical properties of the FO membrane.

In this study, the highly hydrophilic poly(vinylidene fluoride) membrane is superior in FO properties, with a water flux of 17.32 LMH and a reverse solute flux of 4.34 gMH. In addition, an excellent performance of 60.15 LMH and 14.88 gMH can be achieved when the pressure-retarded osmosis (PRO) test mode with a draw solution concentration of 2.0 M is used in the test. It shows that the membrane prepared using the novel method showed excellent FO performance, which has high potential in industrial applications such as desalination.
range of pH values and temperatures. However, one disadvantage of the IP method is that the reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) is difficult to control, leading to the formation of a rough and thick PA layer. In this regard, Stafford’s group proposed an innovative method, termed the molecular layer-by-layer (mLBL) method, to fabricate the PA layer. In this method, the reaction between these two reactive monomers MPD and TMC occurs at the molecular level, resulting in a thinner and flatter PA active layer. Another advantage of the mLBL method is its greater flexibility as it allows the number of layers to be controlled.

Despite being able to produce high-quality films, the mLBL method has some drawbacks. First, it is necessary to hydrolyze the substrate to enable the surface to carry negative charges. A convenient method to accomplish hydrolysis is to soak the substrate in sodium hydroxide (NaOH), but this process would only be suitable for polyacrylonitrile (PAN)-based materials. In addition, when a freestanding PAN substrate was immersed in NaOH, the mechanical strength of the substrate would be reduced, which would negatively influence subsequent processes.

Therefore, we developed a method to prepare a solution, containing dopamine (DA) and GO, in a weakly alkaline environment to negatively charge DA and GO. In general, the DA would be expected to undergo self-polymerization to form polydopamine (PDA). The excellent adhesive properties of the PDA would enable the PDA/GO mixture to be firmly coated onto any substrate, thereby ensuring that the surface is negatively charged. As a result, we proposed a modified mLBL method by replacing the hydrolysis process in the typical mLBL method by coating the membrane surface with PDA/GO. This approach not only maintains the strength of the membrane but also increases the surface hydrophilicity. Additionally, the great surface adhesion properties of PDA would make it possible to apply this method to different substrates.

The purpose of this study is to design a TFC membrane with high water flux ($J_w$) and low reverse flux ($J_r$). This work led us to propose a novel method, the modified mLBL, to fabricate PA active layers on different substrates. In this regard, PAN was first coated onto nonwoven fabric (denoted as the nonwoven PAN substrate) followed by coatings of PDA/GO and polyethylenimine/poly(acrylic acid) (PEIPAA) layers and subsequent PA layer deposition. The processes of applying the PDA/GO, PEIPAA, and PA coatings are collectively referred to as the modified mLBL process. In this work, nonwoven fabric was used as a support to provide sufficient mechanical strength for the FO membrane. This method enables a PA layer to be synthesized on freestanding PAN substrates and different substrates, including hydrophilic poly(vinylidene difluoride) (PVDF), to attain highly hydrophilic PVDF and titania-coated carbon nanotube (TCNT) membranes. The effects of processing parameters of the modified mLBL method on the FO performance using different substrates were investigated. To the best of our knowledge, this is the first time the mLBL method is applied to different substrates to enhance the FO performance.

2. MATERIALS AND EXPERIMENTS

2.1. Materials. The PET nonwoven fabric was provided by the Industry Technology and Research Institute (ITRI), Taiwan. Hydrophilic and highly hydrophilic PVDF substrates (the latter with a pore size of 0.22 μm) were obtained from Finetech and ITRI, respectively. Graphite flakes (325 mesh), potassium permanganate (KMnO₄), and trimesoyl chloride (TMC) (99% purity) were purchased from Alfa Aesar. A TCNT suspension (3 wt % multiwall CNTs in aqueous solution) was purchased from TCNT Corporation. Sulfuric acid (H₂SO₄) with 97% purity, hydrochloric acid (HCl, 37%), dopamine hydrochloride (with average molecular weight (Mₘ) of 329.24), polyacrylonitrile (PAN, with Mₘ of 150 000), polyethylenimine (PEI, with Mₘ of 750 000), polycrylonitrile (PAA, with Mₘ of 100 000), and m-phenylenediamine (MPD) with 99% purity were supplied by Sigma-Aldrich. Toluene, acetone, and isopropanol with 99% purity were obtained from ECHO Chemical Co., Ltd., and sodium chloride (NaCl) was purchased from J.T. Baker Chemical.

2.2. Fabrication of Substrate. In this study, we prepared the following five substrates: hydrophilic PVDF, highly hydrophilic PVDF, nonwoven PAN, freestanding PAN, and TCNT. Apart from the hydrophilic and highly hydrophilic PVDF substrates, which are commercially available, the other three substrates, nonwoven PAN, freestanding PAN, and TCNT substrates, were fabricated according to the following procedures.

The nonwoven PAN substrate was fabricated by first dissolving PAN powder in N-methyl-2-pyrrolidone (NMP) to prepare a 12 wt % PAN cast solution at 60 °C. The mixture was stirred for 6 h until complete dissolution. Second, after degassing the solution overnight, we cast the solution on the nonwoven fabric and immersed it into the coagulation bath filled with tap water, which we designated as the phase inversion method. Subsequently, we prepared a freestanding PAN substrate by replacing the tap water in the coagulation bath with NMP solution to obtain lace structure in the PAN layer followed by a process of casting 12 wt % PAN on a glass plate, which was immediately immersed in the NMP/water solution with a specific concentration. The freestanding PAN substrate was obtained after the phase inversion process. The TCNT membrane was fabricated by casting a suspension of TCNT on the nonwoven substrate followed by drying at 80 °C.

2.3. Preparation of GO and PDA/GO Solution. GO was synthesized from graphite powder via the modified Hummers’ method. Concisely, 1.0 g of graphite powder (325 mesh) was added to 100 mL of concentrated H₂SO₄ and stirred at 10 °C for 1.0 h. Subsequently, 4.0 g of KMnO₄ was slowly added under stirring at 30 °C for 6.0 h. Finally, 150 mL of deionized (DI) water was introduced for dilution and the obtained mixture was centrifuged and rinsed repeatedly with DI water until the solution was neutral. The PDA/GO coating solution was prepared by the dissolution of 1.0 g of dopamine HCl in 500 mL of 10 mM Tris–HCl buffer solution at pH = 8.5 with 20 mg of GO.

2.4. Fabrication of the TFC-FO Membrane. Figure 1 illustrates the processes by which the TFC-FO membrane was synthesized. The prepared nonwoven substrate coated with PAN was immersed in the PDA/GO solution for 4.0 h and then rinsed repeatedly with DI water to remove the unreacted chemicals on the substrate. After coating of the PDA/GO onto the substrate, the negatively charged substrate was soaked in a 0.5 M NaCl aqueous solution containing cationic 0.1 wt % PEI for 15 min, followed by washing with DI water. The substrate onto which PEI was deposited was soaked in a 0.5 M NaCl aqueous solution containing anionic 0.1 wt % PAA for 10 min.
and subsequently rinsed with DI water to complete the construction of the PEI/PAA interlayer.

Finally, the PA active layer was formed on the PEI/PAA-deposited substrate by alternative cross-linking of MPD and TMC. Briefly, the membrane was first dipped in 1 wt % MPD in toluene for 30 s followed by rinsing with acetone to remove the unreacted MPD solution. Afterward, 1 wt % TMC in toluene was poured onto the membrane for 30 s followed by washing with toluene. This process, which is defined as one mLBL cycle, can be repeated several times until the desired number of mLBL cycles has been reached. It should be noted that, after the last cycle, the membrane was exposed to hot air for 10 s at 70 °C to cure the PA layer.

2.5. Film Characterizations and Designation of Sample Names. 2.5.1. Characterization of the TFC-FO Membrane. The morphologies of the membranes were examined by field emission scanning electron microscopy (FESEM, JEOL JSM-8100). The surface roughness was quantified by atomic force microscopy (AFM, BRUKER) using the tapping mode in a selected area of 5 μm × 5 μm. The characteristic chemical bonding of the fabricated TFC membrane was investigated using attenuated total reflection—Fourier transform infrared (ATR-FTIR) spectroscopy in the range of 600–4000 cm⁻¹ using the transmittance mode. The surface hydrophilicity of different surfaces was assessed by measuring the water contact angle (First Ten Ångstroms FTA125). The chemical compositions of the membranes were investigated by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI).

2.5.2. FO Performance of the TFC-FO Membrane. Based on the method proposed by Cath, we built a lab-scale system to evaluate the FO performance of the fabricated TFC-FO membrane.²⁸ The feed (FS) and draw (DS) solutions of this system consisted of DI water (800 mL) and a 1 M NaCl solution (600 mL), respectively. The effective membrane area was 16 cm², and the flow rate for both the FS and DS was 25 cm/s. Each membrane was tested for 2.0 h, and the data collected during the first 30 min were discarded in consideration of system stabilization. The water flux and reverse salt flux were determined based on the data obtained during the remaining 90 min using eqs 1 and 2, respectively.

\[
J_w = \frac{W/p_w}{A_m \Delta t} = \frac{\Delta V}{A_m \Delta t} \tag{1}
\]

\[
J_s = \frac{\Delta (C_V)}{A_m \Delta t} \tag{2}
\]

where \(W\) is the weight increase of DS, \(p_w\) is the density of water, \(A_m\) is the effective membrane area, \(\Delta V\) is the volume change of the DS during the operating time \(\Delta t\), \(C_V\) is the concentration of salt, and \(V_i\) is the volume of the FS.

Salt rejection \(R\) was calculated according to eq 3, using 0.6 M NaCl as the FS and 2.0 M MgCl₂ as the DS.

\[
R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{3}
\]

where \(C_p\) represents the salt concentration in the feed solution and \(C_f\) represents the permeated salt concentration.

2.5.3. Designation of Sample Names. In this study, we used five substrates, as shown in Table 1. For the PAN system, samples were named according to the formula \(\alpha\beta\gamma\delta\varepsilon\zeta\), where \(\alpha\) represents the substrate with or without nonwoven fabric, \(\beta\gamma\delta\varepsilon\zeta\) signifies the ratio of NMP to water in the coagulation bath, \(\delta\) denotes the casting thickness of PAN (μm), and \(\zeta\) represents the PA forming method. For example, Freestanding-9-1PAN300-mLBL3 means that nonwoven fabric was not used, the ratio of NMP to water is 9:1, the PAN casting thickness is 300 μm, and three PA layers were synthesized using the modified mLBL method.

The FO membranes that were fabricated without using PAN were named based on the substrate being used, for example, hydrophilic PVDF, highly hydrophilic PVDF, or TCNT.

### Table 1. Naming of the Samples in This Study

| sample | Supporting Layer Type | PA Forming Method (layer) |
|--------|------------------------|--------------------------|
| Nonwoven-0-1PAN150-mLBL5 | hydrophilic PVDF | modified mLBL5 |
| Nonwoven-0-1PAN150-mLBL3 | highly hydrophilic PVDF | modified mLBL3 |
| Nonwoven-0-1PAN150-mLBL1 | TCNT | modified mLBL3 |
| Freestanding-0-1PAN300-mLBL3 | Freestanding-9-1PAN300-mLBL3 | Freestanding-9-1PAN300-IP |
| Freestanding-9-1PAN300-IP | IP | modified mLBL3 |

3. RESULTS AND DISCUSSION

3.1. Fabrication of Nonwoven PAN Substrate Using the Modified mLBL Method. 3.1.1. Membrane Morphology. Figure 2 shows the morphological variation of the membrane surface during the modified mLBL processes. The surface of the PAN layer contains a large number of nanoscale pores (Figure 2a). After PDA/GO coating, the extruded structure can be observed (Figure 2b), which becomes uniform after coating with PEIPAA (Figure 2c), indicating that the PEIPAA layer can effectively prevent the penetration of MPD and TMC into the supporting layer. Finally, the nodular structure of the PA layer shown in Figure 2d indicates the successful formation of the active layer.²⁹
which are attributed to the C\textsuperscript{\textendash}\textsubscript{H}, C\text{\textendash}\textsubscript{N}, and \text{\textendash}CH\textsubscript{3} bonds, respectively.\textsuperscript{32} The peaks shown in the PDA/GO spectrum are basically the same as those of the PAN substrate except the peak at 2343 cm\textsuperscript{\textendash}1, which is attributed to the O\text{\textendash}C\text{\textendash}O bond resulting from the CO\textsubscript{2} contamination. It is because that the PDA/GO coating layer is too thin to be detected and the typical peaks for PDA cannot be obviously observed in the spectrum. PEIPAA deposition adds additional carboxyl groups to the membrane, leading to the increased intensities of peaks at 3410 cm\textsuperscript{\textendash}1 (O\text{\textendash}H) and 1568 cm\textsuperscript{\textendash}1 (asymmetric C\text{\textendash}\text{\textendash}O stretching of COO\textsuperscript{\textendash}\textsuperscript{\textendash}H),\textsuperscript{31} inferring that the membrane is more negatively charged due to the presence of COO\textsuperscript{\textendash}H. Finally, the three characteristic peaks of PA are 1663, 1609, and 1541 cm\textsuperscript{\textendash}1, which are attributed to the C\text{\textendash}\text{\textendash}O (amideI), N\text{\textendash}H, and \text{\textendash}CO\text{\textendash}NH\textendash\text{\textendash}H bonds, respectively,\textsuperscript{32} indicating the successful formation of the PA layer.

3.1.3. AFM Analysis. AFM was used to study the roughness of the deposited surfaces, and the results are shown in Figure 4. Figure 4a shows a roughness of 11.6 nm for the PA layer. After coating the PA layer with PDA/GO, the surface roughness slightly increases to 14.6 nm due to the presence of extruded GO nanosheets from the PDA. The surface roughness decreases after deposition of the PEIPAA layer, as depicted in Figure 4c. The flatter surface of the deposited PEIPAA layer is beneficial for the formation of the PA layer because the reaction is more homogeneous.\textsuperscript{26} Finally, a high surface roughness of 65.6 nm was determined for the PA, as shown in Figure 4d, which is consistent with the FESEM results.

3.1.4. Contact Angle and XPS Analysis. The water contact angle is used to study the surface wettability of the membrane, as shown in Figure S1, Supporting Information. In Figure S1a, pristine PAN has a water contact angle of approximately 60\degree, with the characteristic of a hydrophilic substrate. After the PDA/GO coating on the PAN surface, which is shown in Figure S1b, the water contact angle decreases to approximately 40\degree, indicating that the PDA/GO coating increases the hydrophilic nature of the membrane, which is favorable for FO application.\textsuperscript{33–36}

XPS is used to quantify the degree of cross-linking of the PA layer. An oxygen-to-nitrogen (O/N) ratio close to 1 indicates that the PA layer is fully cross-linked, whereas an O/N ratio close to 2 indicates that the PA layer is fully linear.\textsuperscript{35} The XPS result shows that the PA layer on the Nonwoven-PAN150- mLBL3 membrane has an O/N ratio of 1.18, suggesting that the PA layer formed by the modified mLBL method possesses a remarkable degree of cross-linking, which is responsible for the good selectivity of the TFC-FO membrane.

3.1.5. Tests of FO Performance. Figure 5a shows the top and cross-sectional views of the PA layer on the Nonwoven-PAN150-mLBL membranes with different coating cycles. The nodular or ridge-valley structure on the surfaces indicates the successful formation of the PA active layer via the modified mLBL method and is independent of the number of mLBL cycles.\textsuperscript{29} Increasing the number of mLBL cycles obviously produces thicker PA layers, as shown in Figure 5a(vi). The thick PA layer is unfavorable for the FO application because of the high resistance for water permeation of the active layer. However, an overly thin PA layer results in low membrane selectivity. Thus, it is necessary to determine the proper number of mLBL cycles required to optimize the FO performance.

As shown in Figure 5b, the FO performance of the membranes prepared by varying the number of mLBL cycles was measured. The results reveal that both the mLBL3 and mLBL5 membranes outperform the mLBL1 membrane in terms of FO performance and the mLBL3 membrane has a higher \(J_s\) than the mLBL5 membrane and an acceptable \(J_w\).
value. Thus, we chose the three-cycle process to prepare the PA active layer by the modified mLBL method for most of the PAN-based membranes.

3.2. Preparation of Freestanding PAN Membrane via the Modified mLBL Method. To increase the value of $J_w^*$, we fabricated a PA layer on freestanding PAN substrates using the modified mLBL method. As shown in Figure 6a, membranes with different PAN casting thicknesses were prepared to investigate their FO performance. Obviously, as the PAN casting thickness decreases, both $J_w$ and $J_s$ increase because the lower resistance of the thinner membrane promotes the exchange of water and solute molecules across the membrane, thereby alleviating the ICP effect.10

We also used the modified mLBL method to fabricate Freestanding-9-1PAN with a lace structure and compared the performance with the FO membrane containing a PA layer formed by the IP method (Figure 6b). The results indicate that the FO properties of the PA layer formed by the modified mLBL method are superior to those formed by the IP method. This is attributed to the presence of the PEIPAA layer, which prevents the PA layer from coming into direct contact with the PAN layer and enhances the flatness of the supporting layer. As a consequence, the PEIPAA layer decreases the mass transport resistance between the active and supporting layers, resulting in a higher $J_w^*$ value. In this regard, a key step during processing is to rinse the surface to remove the MPD and TMC residues after each mLBL cycle. As a result, a dense PA layer can be attained, which provided a lower resistance than that formed by the IP method, thereby improving the selectivity of the membrane.

3.3. Processing of Hydrophilic PVDF, Highly Hydrophilic PVDF, and TCNT Membranes. 3.3.1. Membrane Morphology. In this study, we also employed the modified mLBL method to fabricate FO membranes on different substrates. Figure 7a–c depicts the surface morphologies of different substrates, including the hydrophilic PVDF, highly hydrophilic PVDF, and TCNT substrates. (d–f) High-magnification images of (a–c), respectively.

Figure 5. Morphological images of the TFC membrane prepared using different mLBL cycles: (a) top view and cross-sectional view of PA layer on the Nonwoven-PAN150-mLBL membrane: (i, iv) mLBL1, (ii, v) mLBL3, (iii, vi) mLBL5; (b) FO performance of the Nonwoven-PAN150-mLBL membrane with different mLBL cycles (under FO mode).

Figure 6. FO performances of TFC-FO membrane: (a) different PAN casting thicknesses of Freestanding-0-1PAN6-mLBL3 and (b) different PA forming methods on Freestanding-9-1PAN300-x (under FO mode).

Figure 7. Surface morphologies of the different substrates: (a) hydrophilic PVDF, (b) highly hydrophilic PVDF, and (c) TCNT substrates. (d–f) High-magnification images of (a–c), respectively.
captured a cross-sectional view of the pore structure of the PA layer on the membrane. Based on Figure 7e, the highly hydrophilic PVDF membrane shows high pore continuity, which lowers the resistance for water permeation.

3.3.2. AFM Analysis. Figure 8 shows the surface morphologies of the TFC-FO membranes prepared using different substrates: (a) hydrophilic PVDF, (b) highly hydrophilic PVDF, and (c) TCNT substrate. (d–f) Cross-sectional views of (a–c), respectively.

Figure 8. Surface morphologies of the TFC-FO membranes prepared using different substrates: (a) hydrophilic PVDF, (b) highly hydrophilic PVDF, and (c) TCNT substrate. (d–f) Cross-sectional views of (a–c), respectively.

Table 2. Surface Roughness of the Membranes During The Modified mLBL Process.

| Sample              | Ra (nm) | Rq (nm) |
|---------------------|---------|---------|
| hydrophilic PVDF    | 29.6    | 40.4    |
| after PDA/GO        | 20.7    | 26.6    |
| after PEIPAA        | 14.4    | 18.0    |
| highly hydrophilic PVDF | 101.0  | 131.0   |
| after PDA/GO        | 66.2    | 93.6    |
| after PEIPAA        | 59.6    | 88.7    |
| TCNT                | 56.8    | 73.5    |
| after PDA/GO        | 47.4    | 62.1    |
| after PEIPAA        | 37.8    | 49.7    |

*Ra: roughness, Rq: root mean square.

different substrates, and Table 2 summarizes the surface roughness of different membranes during the modified mLBL process. The morphology depicted in Figure 8e indicates that highly hydrophilic PVDF possesses the largest pore size. Although a large pore size is beneficial for water permeation, an excessively large pore size may cause the PA active layer to easily fracture during the FO test because of less contact area between the supporting and active layers. Therefore, we analyzed the topography of the different membranes after each process by AFM to investigate the surface roughness change during the modified mLBL process. After application of the PDA/GO coating, the surface roughness of all of the membranes decreases because the smooth surface of the GO nanosheets flattens the surface. However, after coating the surface with GO alone without PDA acting as a binder, the GO nanosheets can be easily peeled off from the substrate. On the other hand, exposing the substrate to PDA alone increases the surface roughness because of the presence of GO; thus, both PDA and GO are essential for designing a high-performance FO membrane. The deposition of PEIPAA on the substrate further decreases the surface roughness of the membranes. A flatter membrane surface is beneficial for the PA formation because it enables a more homogeneous reaction.

3.3.3. Contact Angle Analysis. The water contact angles of different membranes are compared in Figure 9a. After PDA/GO coating, the water contact angles of all of the membranes decrease, indicating that PDA/GO increases the hydrophilic nature of the membrane. However, the difference in the water contact angle of these three membranes after PDA/GO coating is insignificant. These results seem to be related to the surface pore size because a large pore size may decrease the ability of a water droplet to stand on the membrane, resulting in a smaller water contact angle. Furthermore, it is noteworthy that during measurement of the contact angle, a water droplet on the highly hydrophilic PVDF substrate disappeared within 16 s, indicating the large pore size and high pore continuity of this substrate.

3.3.4. FO Performance. The FO performance of different membranes was investigated. As shown in Figure 9b, obviously, the highly hydrophilic PVDF membrane exhibits the highest water flux. The water flux is related to the pore size and pore continuity in the supporting layer; therefore, the larger pore size and higher pore continuity promote the efficient exchange of water and salt molecules across the membrane, leading to a milder ICP effect and facilitating water permeation. Among all of the membranes studied in this work, the highly hydrophilic PVDF membrane has excellent FO properties, with a water flux of 17.32 LMH and a reverse solute flux of 4.34 gMH. Furthermore, the salt rejection rate of the highly hydrophilic PVDF membrane is 86.7%, indicating the outstanding salt rejection properties of the membrane.

These excellent FO properties of the highly hydrophilic PVDF-mLBL3 membrane led us to investigate the effect of different DS concentrations on the FO as well as the PRO performance. Figure 10a,b depicts the results in FO mode and PRO mode, respectively. As shown in the figure, under the same operating conditions, the water flux increases with an increase in the DS concentration in both FO and PRO modes owing to the larger osmotic driving force across the membrane. A comparison of $J_w$ values in FO and PRO modes at the same DS concentration shows that the water flux in FO mode is much lower than that in PRO mode because of the greater...
severity of the ICP effect in FO mode. Additionally, at a higher DS concentration, the difference in the water flux between FO and PRO increases due to the more serious salt leakage problem at higher DS concentration, resulting in greater external concentration polarizations (ECP) and ICP effects in FO mode.29 With respect to the reverse salt flux depicted in the figure, the trend of \( J_\text{w} \) is highly similar to that of \( J_\text{d} \) because of the elevated driving force across the membrane with the increase in the NaCl concentration. Nevertheless, all of the values are still acceptable.

As depicted in Figure 10c,d, we compare the performance of our fabricated membranes with that of those prepared by others. The results show that our membranes outperform the commercial HTI membrane in both FO mode (Figure 10c) and PRO mode (Figure 10d). In addition, the results of this study are comparable to those of other studies, indicating the potential of the modified mLBL method for designing TFC-FO membranes.

4. CONCLUSIONS

In this study, we demonstrated that the PA film formed by the modified mLBL method has more advantageous properties than that formed by the IP method, and we found that the use of PDA/GO-coated surfaces not only increases the hydrophilicity of the support membrane but also decreases its surface roughness, thereby facilitating the formation of the PA layer. Moreover, compared to the membrane fabricated using the typical mLBL method involving the PAN layer only, the modified mLBL method is suitable for all kinds of membranes owing to the superior adhesion of PDA. Among all of the TFC-FO membranes fabricated by the modified mLBL method, the highly hydrophilic PVDF membrane has the best FO properties, with a water flux of 17.32 LMH and a reverse solute flux of 4.34 gMH. In addition, an extremely high flux and a reverse solute flux of 60.15 LMH and 14.88 gMH, respectively, can be achieved in PRO mode with 2.0 M DS. Obviously, the TFC-FO membrane prepared using this novel method to fabricate the PA layer has high potential for application in future FO technologies.

**Figure 10.** FO performance of the highly hydrophilic-PVDF-mLBL3 tested with different concentrations of NaCl solution: (a) in FO mode and (b) in PRO mode. Comparison of this work with other TFC-FO membranes: (c) in FO mode and (d) in PRO mode. The red mark shows the results of this study.
(6) Garcia-Castello, E. M.; McCutcheon, J. R. Dewatering press liquor derived from orange production by forward osmosis. J. Membr. Sci. 2011, 372, 97−101.

(7) Yang, Q.; Wang, K. Y.; Chung, T.-S. A novel dual-layer forward osmosis membrane for protein enrichment and concentration. Sep. Purif. Technol. 2009, 69, 269−274.

(8) Zhao, S.; Zou, L.; Tang, C. Y.; Mulcahy, D. Recent developments in forward osmosis: opportunities and challenges. J. Membr. Sci. 2012, 396, 1−21.

(9) McCutcheon, J. R.; Elimelech, M. Modeling water flux in forward osmosis: implications for improved membrane design. AIChE J. 2007, 53, 1736−1744.

(10) Tian, M.; Wang, Y.-N.; Wang, R.; Fane, A. G. Synthesis and characterization of thin film nanocomposite forward osmosis membranes supported by silica nanoparticle incorporated nanofibrous substrate. Desalination 2017, 401, 142−150.

(11) Wei, J.; Qiu, C.; Tang, C. Y.; Wang, R.; Fane, A. G. Synthesis and characterization of flat-sheet thin film composite forward osmosis membranes. J. Membr. Sci. 2011, 372, 292−302.

(12) Wang, Y.; Ou, R.; Ge, Q.; Wang, H.; Xu, T. Preparation of polyethersulfone/carbon nanotube substrate for high-performance forward osmosis membrane. Desalination 2013, 330, 70−78.

(13) Emadzadeh, D.; Lau, W. J.; Matsuura, T.; Rahbari-Sisakht, M.; Ismail, A. F. A novel thin film composite forward osmosis membrane prepared from PSf−TiO2 nanocomposite substrate for water desalination. Chem. Eng. J. 2014, 237, 70−80.

(14) Park, M. J.; Phuntsho, S.; He, T.; Nisola, G. M.; Tijing, L. D.; Li, X.-M.; Chen, G.; Chung, W.-J.; Shon, H. K. Graphene oxide incorporated polysulphone substrate for the fabrication of flat-sheet thin-film composite forward osmosis membranes. J. Membr. Sci. 2015, 493, 496−507.

(15) Yin, J.; Deng, B. Polymer-matrix nanocomposite membranes for water treatment. J. Membr. Sci. 2015, 479, 256−275.

(16) Chen, G.; Liu, R.; Shon, H. K.; Wang, Y.; Song, J.; Li, X.-M.; He, T. Open porous hydrophilic supported thin-film composite forward osmosis membrane via co-casting for treatment of high-salinity wastewater. Desalination 2017, 405, 76−84.

(17) Huang, Z.-M.; Zhang, Y.-Z.; Kotaki, M.; Ramakrishna, S. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. Comp. Sci. Technol. 2003, 63, 2223−2253.

(18) Yan, J.-A.; Xian, L.; Chou, M. Structural and electronic properties of oxidized graphene. Phys. Rev. Lett. 2009, 103, No. 086802.

(19) Hu, M.; Bi, E. Enabling graphene oxide nanosheets as water separation membranes. Environ. Sci. Technol. 2013, 47, 3715−3723.

(20) Perreault, F.; Jaramillo, H.; Xie, M.; Ude, M.; Nghiem, L. D.; Cath, T. Y.; Elimelech, M. Biofouling mitigation in forward osmosis using graphene oxide functionalized thin-film composite membranes. Environ. Sci. Technol. 2016, 50, 5840−5848.

(21) Park, S.-J.; Choi, W.; Nam, S.-E.; Hong, S.; Lee, J. S.; Lee, J.-H. Fabrication of polyamide thin film composite reverse osmosis membranes via support-free interfacial polymerization. J. Membr. Sci. 2017, 526, 52−59.

(22) Johnson, P. M.; Yoon, J.; Kelly, J. Y.; Howarter, J. A.; Stafford, C. M. Molecular layer-by-layer deposition of highly crosslinked polyamide films. J. Polym. Sci., Part B: Polym. Phys. 2012, 50, 168−173.

(23) Jin, W.; Toutianoush, A.; Tiele, B. Use of polyelectrolyte layer-by-layer assemblies as nanofiltration and reverse osmosis membranes. Langmuir 2003, 19, 2550−2553.

(24) Xinpeng, W.; Zhouyi, G. Application of dopamine to sewage treatment and its forecast. Ind. Water Treat. 2015, 7.

(25) Priyadarsini, S.; Mohanty, S.; Mukherjee, S.; Basu, S.; Mishra, M. Graphene and graphene oxide as nanomaterials for medicine and biology application. J. Nanomatt. Chem. 2018, 8, 123−137.

(26) Hegab, H. M.; Elmekawy, A.; Barclay, T. G.; Michelmore, A.; Zou, L.; Saint, C. P.; Ginic-Markovic, M. Effective in-situ chemical surface modification of forward osmosis membranes with polydopamine-induced graphene oxide for biofouling mitigation. Desalination 2016, 385, 126−137.

(27) Hummers, W. S.; Jr; Offeman, R. E. Preparation of graphitic oxide. J. Am. Chem. Soc. 1958, 80, 1339.

(28) Cath, T. Y.; Elimelech, M.; McCutcheon, J. R.; McGinnis, R. L.; Achilli, A.; Anastasio, D.; Brady, A. R.; Childress, A. E.; Farr, I. V.; Hancock, N. T.; et al. Standard methodology for evaluating membrane performance in osmotically driven membrane processes. Desalination 2013, 312, 31−38.

(29) Qi, M.; Wang, J.; He, C. A stable and hydrophilic substrate for thin-film composite forward osmosis membrane revealed by in-situ cross-linked polymerization. Desalination 2018, 433, 1−9.

(30) Gu, J.-E.; Lee, J. S.; Park, S.-H.; Kim, I. T.; Chan, E. P.; Kwon, Y.-N.; Lee, J.-H. Tailoring interlayer structure of molecular layer-by-layer assembled polyamide membranes for high separation performance. Appl. Surf. Sci. 2015, 356, 659−667.

(31) Prusty, G.; Swain, S. K. Synthesis and characterization of conducting gas barrier polycrylonitrile/graphite nanocomposites. Polym. Compos. 2011, 32, 1336−1342.

(32) Tang, C. Y.; Kwon, Y.-N.; Leckie, J. O. Effect of membrane chemistry and coating layer on physicochemical properties of thin film composite polyamide RO and NF membranes: I. FTIR and XPS characterization of polyamide and coating layer chemistry. Desalination 2009, 242, 149−167.

(33) Liu, Q.; Li, J.; Zhou, Z.; Xie, J.; Lee, J. Y. Hydrophilic mineral coating of membrane substrate for reducing internal concentration polarization (ICP) in forward osmosis. Sci. Rep. 2016, 6, No. 19593.

(34) Shen, L.; Hung, W. s.; Zuo, J.; Zhang, X.; Lai, J.-Y.; Wang, Y. High-performance thin-film composite polyamide membranes developed with green ultrasound-assisted interfacial polymerization. J. Membr. Sci. 2019, 570, 112−119.

(35) Ren, J.; McCutcheon, J. R. A new commercial thin film composite membrane for forward osmosis. Desalination 2014, 343, 187−193.

(36) Li, M.-N.; Sun, X.-F.; Wang, L.; Wang, S.-Y.; Afzal, M. Z.; Song, C.; Wang, S.-G. Forward osmosis membranes modified with laminar MoS2 nanosheet to improve desalination performance and antifouling properties. Desalination 2018, 436, 107−113.