Layer-by-Layer Assembly for Preparation of High-Performance Forward Osmosis Membrane

Libin Yang[1], Jinglong Zhang[1], Peng Song[1] and Zhan Wang[2],*

[1]Beijing Key Laboratory for Green Catalysis and Separation, Department of Chemistry and Chemical Engineering, Beijing University of Technology, Beijing, P. R. China.
[2]Beijing Key Laboratory for Green Catalysis and Separation, Department of Chemistry and Chemical Engineering, Beijing University of Technology, Beijing, P. R. China, wangzhan3401@163.com
*Corresponding author

Abstract. Forward osmosis (FO) membrane with high separation performance is needed to promote its practical applications. Herein, layer-by-layer (LbL) approach was used to prepare a thin and highly cross-linked polyamide layer on a polyacrylonitrile substrate surface to prepare a thin-film composite forward osmosis (TFC-FO) membrane with enhanced FO performance. The effects of monomer concentrations and assembly cycles on the performance of the TFC-FO membranes were systematically investigated. Under the optimal preparation condition, TFC-FO membrane achieved the best performance, exhibiting the water flux of 14.4/6.9 LMH and reverse salt flux of 7.7/3.8 gMH under the pressure retarded osmosis/forward osmosis (PRO/FO) mode using 1M NaCl as the draw against a DI-water feed, and a rejection of 96.1% for 2000 mg/L NaCl aqueous solution. The result indicated that layer-by-layer method was a potential method to regulate the structure and performance of the TFC-FO membrane.
Keywords: Forward osmosis; Layer-by-layer; Thin-film composite forward osmosis membrane (TFC-FO), Polyamide.

1. Introduction

In recent years, forward osmosis (FO) have drawn broad attention in wastewater treatment due to the advantages of low energy consumption, weak fouling tendency and high rejection rate [1]. Compared to conventional pressure-driven membrane process, FO is particularly suited to be used in seawater and brine desalination, landfill leachate concentration, industrial waste water recycling and electrical power generation [1, 2]. However, the lack of high performance FO membrane is the major problem hindering its vast application [1]. This is attributed to the intrinsic internal concentration polarization (ICP) occurred in FO, resulting in a decreased osmotic driving force across the membrane with a low permeability. ICP is highly depended on the structures and properties of both the selective layer and the porous substrate [1]. Thus, an ideal FO membrane should be designed with a thin, defect-free selective layer and highly porous substrate to mitigate ICP effect [2].

Up to now, polyamide thin-film composite (PA TFC) membrane is most widely used in FO application due to its excellent perm-selectivity [1]. In addition, this type of membrane is more flexible in structural design as both the selective layer and substrate layer can be designed separately to cater specific needs [1]. The PA selective layer is usually prepared by interfacial polymerization (IP) between amine and chloride monomers [5]. Therefore, different strategies have been used to optimize the IP process, including incorporating of nanoparticles or additives [1, 3] and using additional post-treatments [3]. Although these methods are effective, the intrinsic quick reaction rate of IP results

in the formation of a 200-300 nm polyamide layer on the substrate surface in just a few seconds [3, 4] This greatly limits further optimization of PA selective layer structure and property.

Layer-by-layer assembly method is a more flexible method to prepare polyamide layer with controlled thickness and structure [10]. Kwon et al. used this method to prepare a thin polyamide layer of 30 nm on a porous substrate, and the resultant TFC-FO membrane achieves 200% higher water flux and 70% lower reverse salt flux compared to the IP-assembled membrane [5]. Qi et al. indicated that the performance of the FO membrane can be optimized by regulating the number of the polyeletrolyte bilayers [4]. However, most of LbL-assembled FO membranes are limited in seawater desalination applications, due to their loose selective structure and thus further study should be explored [4].

Herein, we use LbL method to prepare a thin and highly selective polyamide layer on a commercial PAN substrate, and the resultant membrane is expected to achieve high salt rejection and enhanced water permeability than the control TFC-FO membrane prepared by conventional interfacial polymerization (IP). More importantly, the permeation performance of the TFC-FO membrane can be easily regulated by controlling MPD concentration, TMC concentration and the assembly cycles [5]. The morphology and physicochemical property of the resultant TFC-FO membrane were also characterized in detail.

2. Experimental

2.1. Materials
M-phenylenediamine (MPD, 99.5%) was obtained from Aladdin Industrial Corporationin China. Trimesoyl chloride (TMC, 98.0%) was supplied by Sigma-Alorich in United States. Toluene and acetone were purchased from Beijing Chemical Works, China. Sodium hydroxide was purchased from Tianjin Fucheng Corporation, China. PAN substrate membrane with the mean pore size of 0.1μm was supplied by Beijing Ande Membrane Technology, China. The ultrapure water ($\leq 10\mu S/cm$) was prepared by the Millipore Milli-Q ultrapure water system.

3. TFC-FO Membrane Preparation
The membrane preparation process was similar as the literature [10]. The PAN substrate was hydrolyzed in 2M NaOH aqueous solution at 45 °C for 1 h to generate carboxylic group and then rinsed thoroughly with deionized water. Next, the HPAN substrate was immersed in 0.5-2.0 wt. % MPD/toluene solution for 30s and rinsed with acetone. The resulting membrane was then soaked in 0.5-2.0 wt. % TMC/toluene solution for 30s and rinsed with toluene, followed by 120s air drying. These steps were repeated to obtain the desired number of PA layers on the HPAN substrate surface. The obtained TFC-FO membrane was abbreviated as LbL-x, in which x was the number of the repeated cycle.

For comparison, the control TFC-FO was also prepared by interfacial polymerization on the same HPAN substrate. The membrane was first soaked in a 2.0 wt. % MPD aqueous solution for 60s and then the excess MPD solution was poured off. After that, the membrane was immersed into a 0.1 wt. % TMC/hexane solution for 30 s and rinsed with hexane. All the prepared TFC-FO membranes were air-dried in 65 ℃ oven for 5 min and stored in DI-water before use.

4. Characterization of the TFC-FO Membrane

4.1. Membrane Performance in FO Test.
The permeation performance of the TFC-FO membrane was evaluated by a cross-flow system with the effective area of 30 cm^2 using 1M NaCl aqueous solution as the draw and DI-water as the feed solution. The membrane performance was tested in both pressure retarded osmosis (PRO) and forward osmosis (FO) at the cross-flow rate of 25 cm/s and the operating temperature of 20 °C. The water flux (J_w) and the reverse salt flux (Js) of the TFC-FO membrane were calculated according to the reference [3].

4.2. Membrane Performance in RO Test.

The intrinsic separation parameters, including the pure water permeability coefficient A (LMH/bar), salt permeability coefficient B (LMH), salt rejection R (%) and structural parameters (S) of the TFC-FO membrane, were determined by a RO cross-flow filtration system according to the previous literature [3].

5. Analytical Methods

The surface morphologies of the TFC-FO membrane were characterized by a scanning electron microscopy (HitachiS-4300, Japan) and an atomic force microscopy (Pico Scan^{TM} 2500, USA). The chemical compositions of the TFC-FO membranes were performed using a 6700 FTIR spectrophotometer (Nicolet, USA) over a wavenumber range of 400-4000 cm^{-1} at a resolution of 2cm-1. The surface elemental composition of the TFC-FO membrane was characterized by an X-ray photoelectron spectroscopy (XPS, Thermoescalab 250Xi, US) using a monochromatized Al K-α radiation [5].

6. Results and Discussion

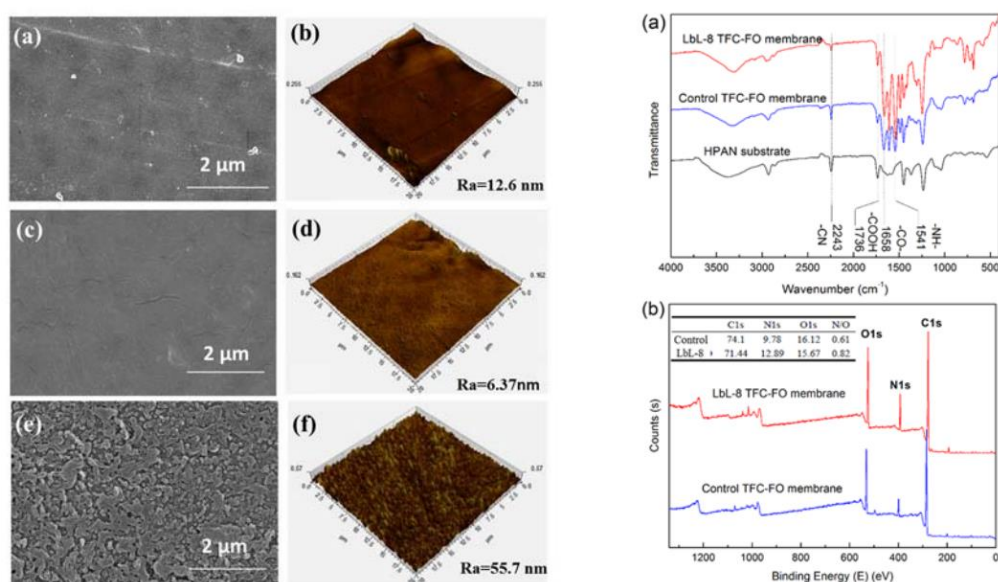*6.1. Characterization of the TFC-FO Membrane*

Figure 1. (a) SEM image and (b) AFM image of the HPAN substrate surface, (c) SEM image and (d) AFM image of the LbL-8 TFC-FO membrane surface, (e) SEM image and (f) AFM image of the control TFC-FO membrane surface (prepared by interfacial polymerization).
Figure 2. (a) FTIR spectra and (b) XPS of TFC-FO membranes prepared by LbL or IP method.

The surface morphologies of different membranes were characterized by SEM and AFM observation (Fig. 1). A porous substrate was observed for the HPAN substrate (Fig. 1(a)). After layer-by-layer assembly or interfacial polymerization of polyamide layer on a HPAN substrate surface, a defect-free surface was obtained (Fig. 1(c) and 1(e)). Moreover, the TFC-FO membrane prepared by LbL assembly showed a smooth surface with a roughness value of 6.37 nm (Fig. 1(d)) while the control TFC-FO exhibited a much rougher surface (Ra: 55.7 nm, Fig. 1(f)). This was attributed to different reaction mechanism. In interfacial reaction, the reaction rate is determined by the diffusion of MPD into the organic (TMC) phase, and quick diffusion rate created a rough surface of the synthesized polyamide layer [1]. On the contrary, MPD and TMC is dissolved in the same solvent phase via layer-by-layer assembly, which avoids MPD migration and forms a smooth polyamide surface [1]. The chemical compositions of the resultant membrane were investigated by FTIR and

XPS analysis. As shown in Fig. 2(a), typical peaks of amide groups were observed at 1658 cm-1 and 1541 cm-1 in the FTIR spectrum of both TFC-FO membranes, which ascribed to C=O stretching vibration and N–H bending vibration [16], confirming the successful formation of polyamide layer on the HPAN substrate surface. XPS spectra in Fig. 2(b) also revealed that the two membranes composed of O, N and C elements. Importantly, the XPS spectrum of LbL-8 TFC-FO membrane showed higher N/O ratio compared to the that of the control TFC-FO membrane, indicating a higher cross-linking degree of the polyamide layer of the LbL-8 TFC-FO membrane [14].

7. Effect of Preparation Conditions on the Performance of the TFC-FO Membrane

7.1. MPD Concentration.
The performances of TFC-FO membranes were tested in both pressure retarded osmosis (PRO) and forward osmosis (FO) mode. As shown in Fig. 3, when the MPD concentration was increased from 0.5 wt.% to 2.0 wt.%, the water flux of the TFC-FO membrane first increased and then decreased, and the maximum water flux of 11.6/7.8 LMH (PRO/FO) was achieved at MPD concentration of 1.5 wt.%. While the reverse salt flux of the TFC-FO membrane first decreased and then increased, achieving the minimum value of 13.8/6.9 gMH (PRO/FO) at the same MPD concentration (1.5 wt. %). At first, the increase in MPD concentration increased the cross-linking degree of the polyamide layer [14], resulting in higher selectivity, a decreased the ICP extent and enhanced water flux of the TFC-FO membrane [1]. However, further increasing of MPD concentration promoted the formation of a dense polyamide layer with a lower permeance (Fig. 3(a)). Thus, MPD concentration of 1.5 wt. % was optimal.
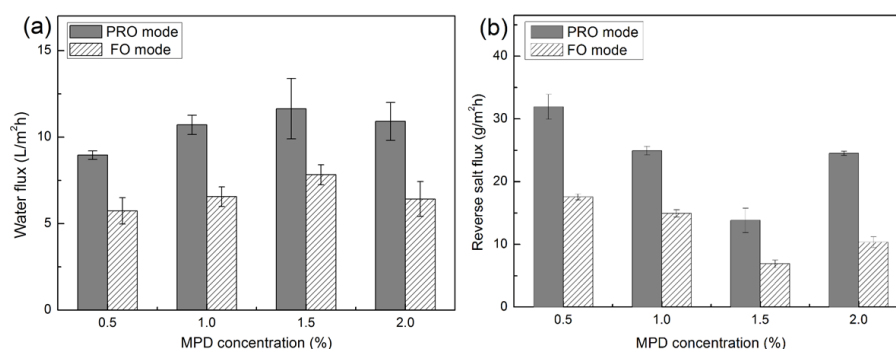

Figure 3. Effect of MPD concentration on the performance of the TFC-FO membrane.

7.1.1. TMC Concentration.
Fig. 4 showed the water flux and reverse salt flux of the TFC-FO membrane at a fixed MPD concentration of 1.5 wt.% and varying TMC concentration (0.5-2.0 wt.%). In the beginning, the water flux of the TFC-FO membrane increased from 6.6/5.1 LMH (PRO/FO) to 10.1/7.4 LMH (PRO/FO) when the TMC concentration was increased from 0.5 wt.% to 1.0 wt.%, along with revere salt flux decreased from 47.7/30.8 gMH to 16.6/10.5 gMH in the PRO/FO mode. The initial increase in TMC concentration enhanced the reaction rate between MPD and TMC and promoted the formation of a highly cross-linked and dense polyamide layer [2]. This decreased the reverse salt passage across the TFC-FO membrane and increased the effective osmotic driving force across [17], thereby achieving the highest water flux of 10.1/7.4 LMH and the lowest reverse salt flux of 16.6/10.5 gMH in the PRO/FO mode at TMC concentration of 1.0 wt.%. However, an excessive high TMC concentration would also decrease the cross-linking degree of PA layer due to the more residual amount of acyl chloride groups on the formed PA layer [18], leading to a decreased perm-selectivity of the TFC-FO membrane at the 2.0 wt.% TMC concentration. Based on the above results, MPD concentration of 1.5 wt.% and TMC concentration of 1.0 wt.% was selected as the optimal condition with a MPD:TMC ratio of 3:2.
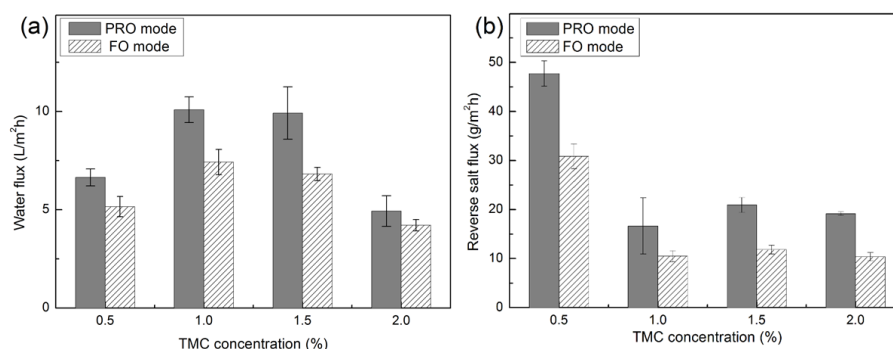
Figure 4. Effect of TMC concentration on the performance of the TFC-FO membrane.

7.1.2. Assembly Cycles. The assembly cycle was also an important factor for TFC-FO membrane preparation process [5]. The thickness of the selective layer should be optimized to ensure a better perm-selectivity for the corresponding TFC-FO membrane [18]. Fig. 5 showed the water flux and reverse salt flux of the TFC-FO membrane with different assembly cycles. The water flux of theTFC-FO membrane increased and the reverse salt flux decreased with the assembly cycle increasing from 2 to 8. The TFC-FO membrane prepared at 8 assembly cycles achieved the maximum water flux of 14.4/7.8 LMH (PRO/FO) and the lowest reverse salt flux of 10.0/5.4 gMH (PRO/FO). This is attributed to the fact that the polyamide layer gradually became denser and thicker with the increasing of assembly layers [5, 18]. This resulted in enhanced the perm-selectivity of the TFC-FO membrane at 8 assembly cycles due to its reduced ICP effect. However, a reduction in water flux and reverse salt flux was observed as assembly cycles were increased from 8 to 10 due to the excessive thicker polyamide layer formed. Thus, the TFC-FO membrane exhibited the best perm-selectivity at 8 assembly cycles.
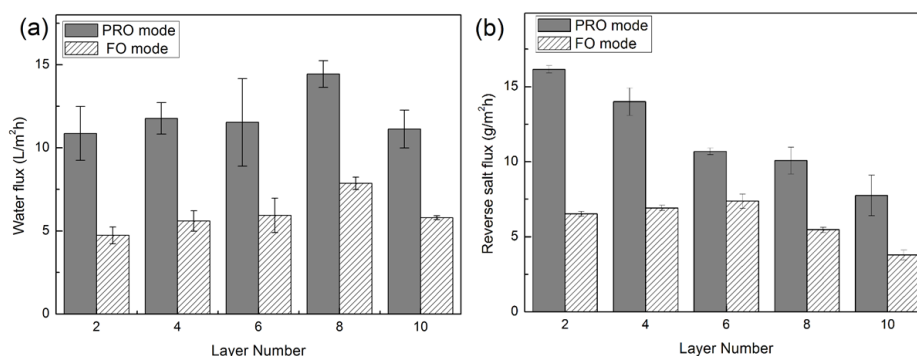

Figure 5. Effect of assembly cycles on the performance of the TFC-FO membrane.

7.2. Performance Comparison of the LbL-assembled TFC-FO Membranesand the IP-assembled TFC-FO Membrane
To further demonstrate the attribute of LbL assembly method, the separation parameters of different TFC-FO membranes including the water permeability coefficient (A), salt permeability coefficient (B), salt rejection (R), structural parameter (S) and water flux (JW) were tabulated in Table 1. The TFC-FO membrane prepared by LbL method at 8 assembly cycles exhibited better FO performance compared to the control TFC-FO membrane in terms of about 80% higher water flux, 8.6% higher salt rejection, 51% lower structural parameter (Table 1). Moreover, the LbL-8 TFC-FO membrane also showed a high rejection of 96.1% for NaCl aqueous solution and a low B/A value of 0.28, reflecting improved selectivity of the polyamide layer [7]. In brief, LbL method endowed the TFC-FO membrane with enhanced perm-selectivity and mitigated ICP effect, which can be used a facile and promising method to regulate the structure and performance of the TFC-FO membrane.

Table 1. Pure water permeability coefficient (A), salt permeability coefficient (B), salt rejection (R), structural parameter (S) and water flux (JW) of TFC-FO membranes.

Membrane ID	A (LMH/bar)	B (LMH)	R(%)	B/A (bar)	S (μm)	JW(LMH) PRO/FO
Control	0.98 ±0.02	0.84 ±0.05	87.5 ±0.9	0.85	3063	8.3/4.2
LbL-2	1.46 ±0.14	2.16 ±0.30	78.6 ±1.1	1.48	2941	10.9/4.7
LbL-4	1.34 ±0.09	1.39 ±0.08	83.2 ±0.2	1.03	2354	11.7/5.6
LbL-6	1.27 ±0.06	1.02 ±0.14	86.8 ±1.5	0.80	2153	11.5/5.9
LbL-8	1.09 ±0.03	0.31 ±0.04	96.1 ±1.4	0.28	1514	14.4/7.8
LbL-10	1.15 ±0.03	0.15 ±0.04	98.2 ±0.6	0.13	2206	11.3/5.8

8. Conclusions

In summary, a high perm-selectivity TFC-FO membrane was successfully prepared via layer-by-layer assembly (LbL) of polyamide layer on a hydrolyzed polyacrylonitrile (HPAN) substrate. A smooth, dense and highly selective polyamide layer was obtained via LbL method, which is beneficial to enhance selectivity and mitigate ICP extent of the TFC-FO membrane. Importantly, the separation performance of the resulting TFC-FO membrane can be easily regulated by varying monomer concentrations and assembled cycles. The optimal preparation condition was 8 assembly cycles, 1.5 wt. % MPD concentration and 1.0 wt.% TMC concentration. The corresponding TFC-FO membrane achieved around 80% higher water flux, 8.6% higher salt rejection (NaCl) and 51% lower structural parameter compared to the control TFC-FO membrane prepared by interfacial polymerization. Therefore, LbL assembly method can be used as a promising approach for regulating the physicochemical property of polyamide layer and the perm-selectivity of resultant TFC-FO membrane in facile way.

9. Acknowledgements

10. References

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