Synthesis and characterization of thin film nanocomposite forward osmosis membrane with hydrophilic nanocomposite support to reduce internal concentration polarization

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ABSTRACT

Realizing that one of the most important challenges in the forward osmosis (FO) membrane is internal concentration polarization (ICP), thin film nanocomposite (TFN) membranes were prepared by incorporating different loadings of titanium dioxide (TiO$_2$) nanoparticles (ranging from 0 to 0.90 wt%) into the polysulfone (PSf) substrate in order to reduce ICP. The nanocomposite substrates prepared were characterized with respect to hydrophilicity, overall porosity, surface roughness and cross-sectional morphology by different methods. Results revealed that both hydrophilicity and porosity of the substrate were increased upon addition of TiO$_2$ nanoparticles. Moreover, a large number of finger-like macrovoids were developed by increasing the loading of TiO$_2$ nanoparticles, leading to enhancement in water permeability. As for the FO performance tested at AL-FS orientation and with DI water as feed and 0.5 M NaCl as draw solution, the TFN membrane prepared using PSf substrate embedded with 0.60 wt% TiO$_2$ nanoparticles (designated as TFN0.60) exhibited the most promising result by showing water flux of 18.81 L/m^2 h, i.e. 97% higher than the control TFC membrane prepared by substrate without TiO$_2$ incorporation (designated as TFC), with no significant change in reverse solute flux. Compared to the control TFC membrane, the FO water flux of TFN0.60 was also reported to increase significantly from 4.2 to 8.1 L/m^2 h (AL-FS orientation) and from 6.9 to 13.8 L/m^2 h (AL-DS orientation) when seawater was used as feed solution and 2 M NaCl was used as draw solution. The increase in water flux can be attributed to the decrease in structural parameter (S value=0.39 mm), mainly due to the formation of finger-liked macrovoids that connect the top and bottom layer of the substrate and reduce the tortuosity, resulting in decreased ICP. Although further increasing TiO$_2$ nanoparticles loading to 0.90 wt% could increase membrane water permeability, the FO performance was compromised by a significant increase in reverse solute flux. To the best knowledge of the authors, this is the first report on TFN membrane using PSf-TiO$_2$ nanocomposite substrate for FO applications.

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1. Introduction

Today, forward osmosis (FO) process is drawing increasingly stronger attention in many areas such as brackish water [1,2], seawater desalination [3–5], wastewater treatment [6–8], liquid food processing [9–11] and power generation [12,13] due to its low hydraulic pressure requirement. As a result, FO offers an enormous opportunity as a separation process of low energy consumption

and a novel power generation technology. In particular, over the past several years, FO, a membrane-based technology, has attracted considerable attention among membrane scientists as a potential desalination process to compete with reverse osmosis (RO) in the future [5]. This phenomenon can be reflected by the significant growth of research publications in the field of FO in the past 2–3 years [14]. Unlike RO, which uses pressure as the driving force, the driving force in FO is naturally created by the osmotic pressure, which can be achieved by placing a higher osmotic pressure solution (draw solution) on the permeate side of the membrane. Because of this principle of operation, the energy consumption in FO is considerably lower. Another advantage of applying low operating pressure in FO process is the reduced

fouling tendency which might decrease the frequency of cleaning processes and possibly extend membrane lifespan [15,16].

Despite the distinct advantages offered by FO in the water desalination process, the research on how to further improve the properties of the thin film composite (TFC) FO membrane, particularly at the top active skin layer, still remains as main focus of researchers. In 2012, Ma et al. [17] incorporated NaY zeolite nanoparticles into a polyamide (PA) layer made of MPD and TMC monomers for preparing thin film nanocomposite (TFN) membranes for FO applications. The results revealed that with only 0.1 wt/v% zeolite loading into the PA layer, an optimized TFN membrane could be produced by showing water permeability higher than that of typical TFC membrane. The enhanced water permeability is attributed to the sub-nanometer pores in the zeolite nanoparticles, creating a narrow size of channel for water molecules to pass through. In addition to this, other approaches to modify the properties of the PA selective layer for better FO performances include: introducing silver into PA layer [18], changing amine/acyl chloride monomer concentration during IP process [19]. As the TFC FO membrane consists of top PA selective layer and microporous substrate layer, both layers can be independently optimized to achieve desired FO performance [20].

Although FO process presents less fouling, due to low pressures applied on the membrane surface, it is demonstrated to be more sensitive to internal concentration polarization (ICP) than RO [21–25]. ICP generates large boundary layer within the support layer that affects membrane performance [24]. It is generally agreed that small structural parameter S (thickness $\times$ tortuosity/porosity) is highly preferable for a substrate layer in order to minimize the ICP during FO process [21]. In addition, a substrate with greater hydrophilicity may also reduce the water transport resistance, leading to increased water productivity. However, it must be noted that the substrate must make a compromise between high pore size/high flux for avoiding additional resistance to mass transport, and low pore size/low flux for providing a smooth transition to the top PA layer [26]. There are a number of papers concerning ICP phenomena. For example, Wei et al. in 2011 produced a flat sheet TFC FO membrane with a unique structure which was composed of straight finger-like under a thin sponge-like layer using PSf as the substrate [27]. They reported that straight finger-like structures help to reduce the ICP level in the FO test. Bui et al. recently developed a type of nanofiber TFC FO membrane using electrospinning and interfacial polymerization (IP) technique. Their nanofiber TFC FO membrane improved FO efficiency because it not only had low tortuosity but also had high porosity that dramatically reduced the parameters of the membrane structure [28]. However, the mechanical strength of the nanofiber support layer was much lower compared to a typical flat sheet TFC membrane. Furthermore, the good interaction between the nanofiber substrate and PA selective layer presents challenges.

In recent years, it has been reported that inorganic nanoparticles could be potentially used as fillers to improve the properties of microporous ultrafiltration (UF) membranes [29–31] with respect to water permeability, fouling propensity, mechanical and thermal properties, provided the quantity of nanoparticles added was not excessive. Among the nanoparticles studied, titanium dioxide (TiO$_2$) nanoparticle is the most widely used nano-material in preparing nanocomposite membranes [32]. The super hydrophilic surface of TiO$_2$ nanoparticle coupled with its extremely small particle size (< 21 nm) are the main features to be seriously considered for making nanocomposite membrane [33]. However, it is still not very clear to what extent the changes in the typical polysulfone (PSf) substrate properties upon addition of TiO$_2$ nanoparticles would influence the ultimate performances of TFN FO membranes.

One of the objectives of this study is to investigate the effect of the loading of TiO$_2$ nanoparticles incorporated in the PSf substrate of the composite membrane on the properties of the substrate. Another objective is to examine how the changes in the substrate morphology could affect the ICP, followed by structure parameter (S value) and eventually the performance of the TFN membrane when used in FO process.

2. Experimental

2.1. Materials

Polysulfone Udel P-1700 in pellet form (Solvay Advanced Polymers), N,N dimethylformamide (DMF, $> 99.5\%$, Merck), 1-methyl-2-pyrrolidinone (NMP, $> 99.5\%$, Merck) and polyvinylpyrrolidone (PVP K30, Sigma-Aldrich) were used for fabrication of the membrane substrate. 1,3-Phenylenediamine (MPD, $> 99\%$, Merck) and trimesoyl chloride (TMC, $> 98\%$, Merck) were the monomers used for the synthesis of the PA selective layer for TFC membranes. Titanium dioxide nanoparticles (TiO$_2$, Degussa P25, Evonik) were used for modifying substrate properties. Sodium chloride (NaCl, $> 99.5\%$, Merck) was used for preparing salt solution at different concentrations for both FO and RO experiments. Other chemicals used in this study were analytical grade and were used as received without further purification.

2.2. Flat sheet TFN FO membranes

2.2.1. Preparation of FO substrate

The FO substrates were fabricated using PSf dope solutions containing 16.5 wt% PSf, 62 wt% DMF, 21 wt% NMP, 0.5 wt% PVP and different loading of TiO$_2$ nanoparticles (i.e. 0, 0.30, 0.60 and 0.90). To make a dope solution, an appropriate amount of TiO$_2$ nanoparticles was first added into the DMF and NMP mixed solution. This solution then underwent 30 min ultrasonication to minimize TiO$_2$ agglomeration, followed by adding PVP into the mixture prior to PSf addition. The homogenous dope solution prepared was left at 25 °C for 24 h to remove air bubbles trapped within the dope solution. Afterward, the membrane was cast on a glass plate with a casting knife setting the gate height to 140 μm, followed by immersion into a water coagulation bath for phase inversion process to take place. Once the membrane was peeled off from the glass plate, it was transferred to another water bath and further immersed for at least 24 h to remove residual solvent before it was ready for TFN FO membrane preparation. These substrate membranes are hereafter coded as PSf, PSf0.30, PSf0.60 and PSf0.90, depending on the TiO$_2$ loading in the casting dope.

2.2.2. Preparation of polyamide rejection layer

The active rejection layer of TFN FO membrane was prepared via IP process between MPD and TMC on the surface of a pre-cast PSf as shown in Fig. 1. The PSf substrate was heated in a 70 °C ultrapure water bath for 120 s and before it was cooled down to the ambient temperature, the IP process was immediately carried out. At first, 50 ml of 2% (w/v) MPD aqueous solution was poured onto the top of PSf substrate surface and the solution was held on the surface for 2 min to ensure the penetration of MPD monomer in the pores of substrate. The excess MPD solution was then drained off from the substrate surface and the residual droplets of MPD solution were further removed by a rubber roller, followed by pouring 50 ml of 0.15% (w/v) TMC in hexane solution onto the substrate surface. The TMC solution was then drained off from the surface after 1 min contact time. In order to remove unreacted monomers from the TFN membrane surface, the membrane was rinsed with pure n-hexane and dried at ambient condition for