

Novel Thin Film Nano-Composite Forward Osmosis Membranes Prepared on a Support with In Situ Embedded Titanium Dioxide to Reduce Internal Concentration Polarization

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This paper aims at thin-film nano-composite (TFN) FO membrane synthesis by optimizing nano-TiO₂ particles in-situ incorporation concentration. 0.01 wt%, 0.03 wt%, 0.1 wt% and 0.3 wt% concentration of hydrophilic anatase nano-TiO₂ were added into the phase inversion water bath, respectively. The results showed that with the increase of the concentration of nano-TiO₂ particles, the amount of nanoparticles attached to the surface and inner pores of the polysulfone support substrate increased, the dispersion of nanoparticles on the surface of the membrane improved. Moreover, the modified membrane crosslinking degree decreased compare to the control-membrane. Besides, with the increase of the concentration of nano-TiO₂ particles, the water flux of the membrane increased first but then decreased, and the reverse solute flux showed an upward trend. When 0.1 wt% TiO₂ was added in the water bath, the water flux of membrane was highest of all the modified membrane (8.25 L m⁻² h⁻¹) indicating that internal concentration polarization of the membrane was lowest. In conclusion, the optimal concentration of nano-TiO₂ particles for in-situ incorporation was 0.1 wt% due to its high membrane permeability and low internal concentration polarization.

1. Introduction

Population explosion today is placing great stress on energy and clean water across the globe. Water crisis is now a big problem that every country must face. Currently, reverse osmosis and thermal distillation are the most common ways to solve water crisis, which are not conducive to energy conservation. Besides, these two process would both produce concentrated brine which brings harmful impact on environment (Lu et al., 2016). Forward osmosis (FO) process driven by the osmotic pressure difference (unlike RO uses pressure as driving force) across a semi-permeable membrane allows water molecules transfer but rejects solutes, which possesses many advantages like low energy consumption, efficient water recovery, low membrane fouling propensity. Thus, FO is considered as an alternative to reverse osmosis (RO) as a low-cost and more environmentally friendly technology addressing the two issues.

Despite the unique advantages offered by FO in water desalination process, the lack of effective membranes hindered the FO process development. To improve the performance of FO membrane, lots of studies focused on this case were performed such as phase inversion, thin-film polyamide composite (TFC-PA) and layer-by-layer, and so on (Lee et al., 2014). Generally, an ideal FO membrane should meet the following requirements: (1) an ultrathin active layer with high water permeability as well as solute rejection, (2) a porous and hydrophilic support layer with proper water transport and minimized internal concentration polarization (ICP). Considering the two different tailorable components of TFC membranes, the porous support layers are often modified by nano-particles like titanium dioxide (TiO₂), carbon nanotube, porous zeolite particles and graphitic carbon nitride to enhance FO performance (Ma et al., 2013, Ong et al., 2015, Wang et al., 2013). To be more specific, these incorporated nano-particles increased the support layers hydrophilicity and/or porosity, which significantly improved the water transfer process of the TFC membranes in the meanwhile lowered the

effect of ICP by reducing the structural parameters ($S = \text{thickness} \times \text{tortuosity/porosity}$) (Ong et al., 2015). Among the nanoparticles studied, TiO_2 nanoparticle is the most widely used in fabricating TFC membranes (Liu et al., 2013). The hydrophilic nature of TiO_2 nanoparticles coupled with their ultra-small particle size (<21 nm) are the main reasons carefully considered for fabricating nanocomposite membrane. Emadzadeh et al (2014) studied the changes TFC FO membranes properties when different contents of TiO_2 nanoparticles were directly blended into the substrate dope. Even though the improved FO membrane performance was found in this work, but too high concentrations of TiO_2 nanoparticles have a strong tendency to agglomerate in the dope solutions, therefore, this drawback limited the utilization in enhancing FO membrane performance. Recently, Dong et al. (2015) found that zeolite nanoparticles could be uniformly embedded to the polysulfone ultrafiltration (UF) membrane surface by employing the in situ embedment approach, which helped to avoid substantial particle agglomeration and achieve high water permeability. Inspired by this work, the TiO_2 nanoparticles were first used to be embedded into polysulfone membranes serving as an ideal support layer for further fabrication of high-performance FO membranes with no need of dispersing nanoparticles in either monomer solution. As a result, TiO_2 nanoparticles became an integral part of the active layer and the active layer structure, the novel FO membrane would have an enhanced water permeability with little compromise of the rejection performance. Therefore, we report this innovative approach to the fabrication of TFC FO membranes in this paper. To our best knowledge, this is the first study on the support layer with in situ embedded titanium dioxide for improving FO performance.

2. Experimental

2.1 Materials

Polysulfone beads (PSf, average molecular weight (MW) ~22 kDa, Aldrich, USA), polyvinylpyrrolidone (PVP, average MW ~10kDa, Sigma-Aldrich, USA), 1-methyl-2-pyrrolidinone (ACI Labscan, Thailand), 1-methyl-2-pyrrolidinone (NMP, 99%, RCI LABSCAN LIMITED, Thailand). 1,3,5-Benzenetricarbonyl chloride (TMC, Alfa Aesar®, England ,98%), m-Phenylenediamine flakes (MPD, Sigma, America), hexane, (Univar, Redmond, WA). Titanium dioxide (99.8%, 10-25nm, Aladdin, China). For membrane performance tests, sodium chloride (NaCl, ACS reagent) was dissolved in deionized water (DI) obtained from a Milli-Q ultra pure water purification system (Millipore, Billerica, MA).

2.2 Material

A desired micro-structure substrate was fabricated using PSf-PVP mixed casting solution. To prepare the casting solution, a mixed solvent system containing 15 g PSf, 8 g PVP and 77 g NMP was magnetically stirred for 24 h and then left standing for about 12 h at room temperature for degassing (Wang, 2017). A thin film ($195 \pm 10 \mu\text{m}$) of the obtained cast solution was cast onto a clean and smooth glass plate by a membrane casting knife (RK Print Coat Instruments Ltd., UK). The whole composite was exposed in the air for about 10 s before it was immersed into a 60 °C DI water bath for 30 min to initiate the phase inversion. Afterwards, the membrane was removed from the water bath, thoroughly rinsed with Milli-Q water and then transferred to a 4 °C DI water bath for storage and later use. In order to investigate the optimal concentration FO membrane synthesis, nano- TiO_2 with concentrations of 0, 0.01 wt%, 0.05 wt%, 0.1 wt%, and 0.3 wt% were added to the water bath, respectively. Afterwards, the bath solution was sonicated for 1h to ensure the nanometer well-dispersed. The as-prepared membranes thus were designated as PSf-0, PSf-0.01, PSf-0.05, PSf-0.1, and PSf-0.3, respectively. The as-prepared substrates were immersed in the MPD solution for 5 min to ensure complete soaking, then the excess solution was removed by slowly moving an air-knife (Cincinnati, Ohio USA) from one end to the another side within 30 s. Then, the substrate was dipped in TMC solution (0.15 wt% in hexane) for 60 s, to initiate interfacial polymerization. Next, the substrate was taken from the hexane organic phase and set vertically for 2 min to evaporate excess organic solution. Afterwards, a dry curing process was proceeded by putting the as-prepared substrate into an oven at a temperature of 90°C for 5 min. Finally, the obtained composite membranes were washed and stored in 4 °C DI water until they were tested. These resultant membranes were denoted as TFN-0.01, TFN-0.05, TFN-0.1, TFN-0.3, respectively, containing 0.01, 0.05, 0.1 and 0.3 wt% of TiO_2 in water bath, respectively. Apart from this, conventional TFC-PA membrane formed by MPD/TMC (denoted as TFC-0) was also prepared as benchmark.

2.3 Measurement Index and Method.

Water flux and reverse solute flux are both important indexes for forward osmosis, whose calculate formulas and details were reported in our previous work (Wang, 2017). The value of specific reverse solute flux was calculated by the ratio of reverse solute flux and water flux representing the efficiency of forward osmosis. The specific reverse solute flux calculation formula of forward osmosis is as follows: $F_s = J_s/J_w$, where F_s is specific reverse solute flux (mMol/L); J_s is solute flux (mmol/m² h); where J_w is the water flux (L/m² h).

3. Result and Discussion

3.1 Effect of In-situ Incorporation of TiO₂ Concentration on Membrane Surface Morphology

Figure 1(a) shows the surface SEM images of the polysulfone-based membrane when different TiO₂ concentrations were in-situ embedded. It can be seen that as the incorporation concentration increased, the morphology the surface of the substrates were significantly altered. When the incorporation concentration was 0.01 wt%, sporadic nano-TiO₂ particles could be observed on the top surface of the substrate membrane. When the incorporation concentration was increased to 0.05 wt%, the amount of nano-TiO₂ particles on the surface of the membrane increased and showed uneven distribution, as the concentration kept increasing to 0.1 wt%, the amount of nano-TiO₂ particles were further increased, showed evenly distributed planar. Finally, the concentration was increased to 0.3 wt%, the membrane surface was not only fully covered by nano-TiO₂ and a small amount of aggregation phenomenon was observed. Figure 1(b) are SEM images of the active layers of TFN series forward osmosis composite membranes formed by the interfacial polymerization of PSf substrates membrane. The figure showed that the surface of the membrane active layer has a typical valley-mountain structure. However, with the increase of the content of nano-TiO₂ particles on the substrate membrane, the morphology of the forward-permeation composite membrane formed was different: When the concentration was low (0.01 wt%), the formed polyamide layer morphology has no significantly change. When the concentration of TiO₂ concentration was properly increased (0.05 wt%, 0.1 wt%), the polyamide layer morphology became more compact and sharp with small "cracks", however, when the TiO₂ concentration was too large (0.3 wt%), the "valley-ridge" structure on the surface of the polyamide layer became smaller, and the number of "cracks" increased. This may be because when the concentration of TiO₂ was relatively low, the loading particles on the PSf matrix were too small, and the sporadic nano-TiO₂ cannot significantly change the adhesion state of the interfacial polymerization aqueous solution on the surface, and when the concentration of TiO₂ increased, the surface of the PSf substrate was over-loaded. The amount of nano-particles also increased as well as the hydrophilicity of the membrane, so that the aqueous phase solution that penetrates and attaches to the surface during the interfacial polymerization process increased, and the interfacial polymerization process was thus strengthened, but when the TiO₂ content is too much, the TiO₂ in the reaction zone would affect the polyamide structure, which is not conducive to the formation of the characteristic structure. Figure1(c) shows the SEM images of the TFN forward osmosis composite membrane support layer modified by in-situ incorporation at different concentrations. It can be seen that the amount of nano-TiO₂ supported on the membrane support layer varies with the incorporation process concentration increasing. When the incorporation concentration was low (0.01 wt%), the loaded TiO₂ concentration was low, only a small amount of nano-TiO₂ particles can be observed on the bottom surface of the membrane. As the incorporation concentration was appropriately increased from 0.05 wt% to 0.1wt%, the content of nano-TiO₂ loaded on the bottom surface of the film increased, showing a uniform dispersion state. At this time, nano-TiO₂ can also be observed in the pores, and caused their significant reduction. When the incorporation concentration was too high (0.3 wt%), the load of nano-TiO₂ particles on the bottom surface increased continuously, but the particles agglomerations state occurs. The nano-TiO₂ particles in the pores appeared to be "plugging". This may be due to the rapid exchange of the solvent phase (N-methylpyrrolidone) and the non-solvent phase (water) during the phase inversion to form the support layer, and the in-situ incorporation of nano-TiO₂ particles in the non-solvent phase in two phases. When exchanged, nano-TiO₂ particles were embedded in the polysulfone (PSf) layer, so nanoparticles appeared in the bottom of the support layer and in the pore structure. Compared with the pure water non-solvent phase, the in-situ incorporated aqueous phase added with nano-TiO₂ particles has a faster water diffusion rate during the phase inversion process, and it is easier for the polysulfone membrane to form pores.

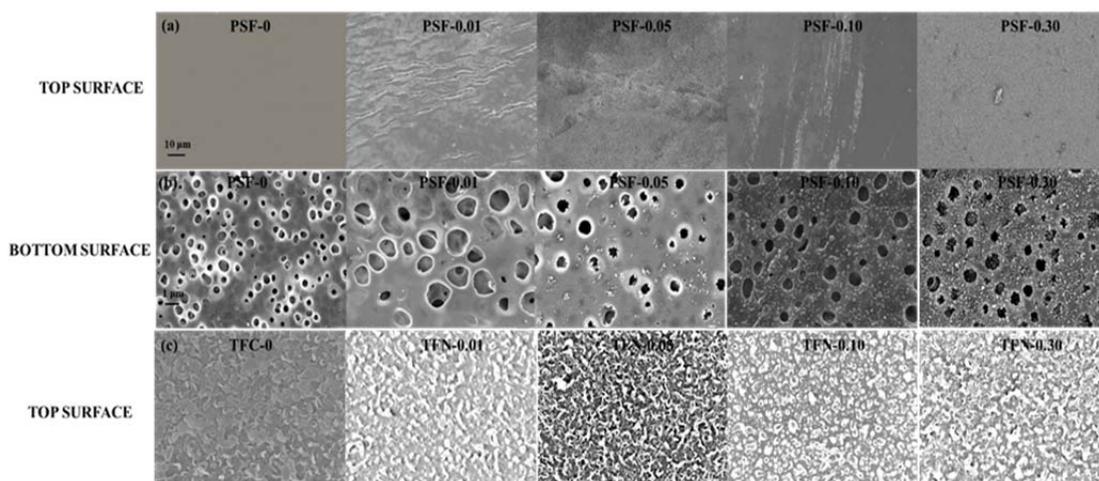


Figure 1: SEM micrographs for top surfaces and bottom surfaces of PSf substrates, and top surfaces of TFC and TFN membranes with different TiO₂ loadings

3.2 Effect of In-situ Incorporation of TiO₂ Concentration on Membrane Chemical Properties

Figure 2a is a Fourier transform infrared spectroscopy (FTIR) test result of an in-situ incorporated polysulfone (PSf) based membrane. As can be seen from figure that the polysulfone (PSf) features regardless of the incorporation concentration. Peaks were observed in the infrared spectra: Symmetry O at $\sim 1150\text{ cm}^{-1}$ = S = O peak, $\sim 1300\text{ cm}^{-1}$ and asymmetric O = S = O peak, and $\sim 1250\text{ cm}^{-1}$ symmetrical COC peak, CH₃-C-CH₃ peak at $\sim 1500\text{ cm}^{-1}$, respectively. However, when compared with the unmodified support layer, the polysulfone membrane incorporated with nano-TiO₂ has no significant change in the absorption peak, which indicates that the in-situ incorporation modification does not change the chemical functional groups of the membrane support layer itself. Figure 2b shows the results of the FTIR test of a forward osmosis composite membrane based on an in-situ incorporated polysulfone membrane for interfacial polymerization. Compared with Figure 2a, there are three distinct peaks: $\sim 1612\text{ cm}^{-1}$ represents the absorption peak of aromatic ring, the absorption peak of $\sim 1662\text{ cm}^{-1}$ amide I bond (C=O), and the absorption peak of $\sim 1542\text{ cm}^{-1}$ amide II bond (CH). These three characteristic peaks indicated the successful of interfacial polymerization process. It has been successfully performed on the surface of polysulfone base film, and it can be seen that the specific absorption peak of polysulfone base film also exists, indicating that the interfacial polymerization does not change the nature of the base film itself, but the positive penetration at different incorporation concentrations. The absorption peak of the active layer of the composite membrane was not significantly different, indicating that in-situ incorporation of nano-TiO₂ particles does not affect the chemical structure of the membrane active layer.

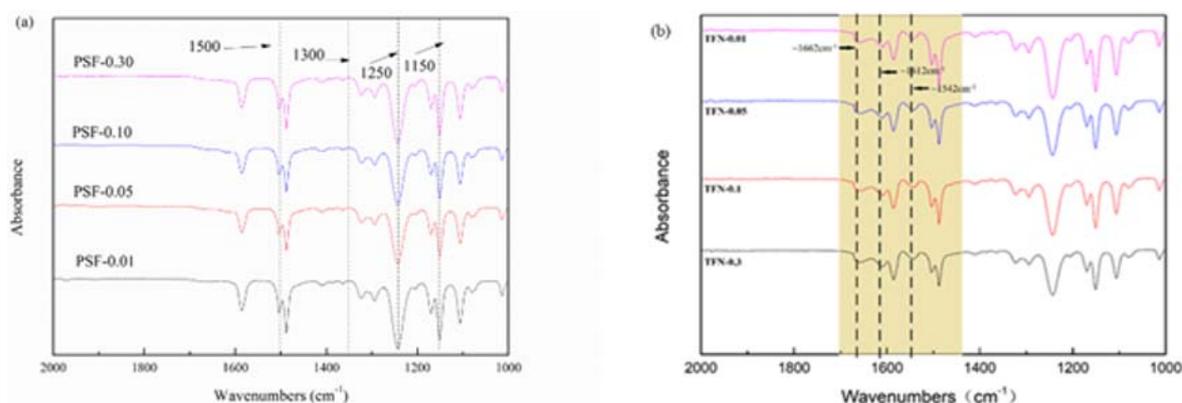


Figure 2: FTIR spectra for PSf substrate (left) and TFN membranes (right) with different TiO₂ loadings

3.3 Effect of In-situ Incorporation of TiO₂ Concentration on FO membrane performance

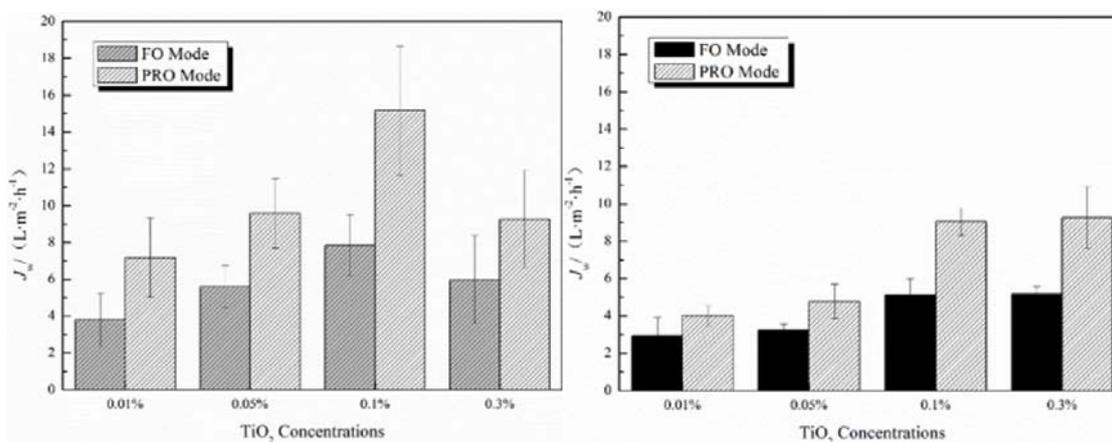


Figure 3: The influence of TiO₂ incorporation concentrations on FO water flux (left) and reverse solute flux (right). The FO performance was tested in active layer-feed solution AL-FS and AL-DS mode with 1.0 M NaCl as draw solution and DI water as the feed solution

As can be seen from the figure, with the increase of the in-situ incorporation concentration, the pure water flux of the forward permeation composite membrane first increased and then decreased: When the incorporation concentration was 0.01 wt%, the pure water flux of the forward permeation composite membrane was 3.81 L·m⁻²·h⁻¹ (FO mode) and 7.18 L·m⁻²·h⁻¹ (PRO mode), respectively; When the incorporation concentration was 0.05 wt%, the as-prepared forward osmosis composite membrane pure water the flux was 5.60 L·m⁻²·h⁻¹ (FO mode) and 9.58 L·m⁻²·h⁻¹ (PRO mode); when the incorporation concentration went up to 0.1 wt%, the pure water flux was 8.25 L·m⁻²·h⁻¹ (FO mode) and 15.17 L·m⁻²·h⁻¹ (PRO mode); when the incorporation concentration was 0.3 wt%, the pure water flux of the composite membrane was reduced to 5.98 L·m⁻²·h⁻¹ (FO mode) and 9.27 L·m⁻²·h⁻¹ (PRO mode). It can be seen that when the incorporation concentration was 0.1 wt%, the pure water flux reached its highest point. According to the above morphological and chemical structure analysis, it can be seen that when the incorporation concentration was low (0.01 wt%), there was a turning-point on the surface of the forward osmosis membrane. The distribution of nano-TiO₂ particles altered the hydrophilicity of the membrane increases slightly, and the water molecules were easy to interact with the membrane; when the incorporation concentration was moderate (0.05 wt%, 0.1 wt%), the surface of the modified forward-infiltrating composite membrane support layer and the pores were covered with a certain amount of nano-TiO₂ particles. These nanoparticles greatly increased the hydrophilicity of the support layer surface, strengthened the affinity of the membrane for water molecules, and at the same time the surface roughness of the active layer formed by the membrane becomes significantly larger, making the activity more active. The contact area between the layer and the solution increased, facilitating the water transfer process; However, when the incorporation concentration is too large (0.3 wt%), the incorporated nano-TiO₂ particles will continue to increase the hydrophilicity of the support layer and the roughness of the active layer, but the nano-TiO₂ particles have accumulated in the pores of the support layer which resulted in the pore blocking phenomenon, the aggregates occupy most of the space of the channel, reducing the diffusion channels of the water, and causing the flux to reduction. It can be seen that as the in-situ incorporation concentration increased, the reverse solute flux of the forward osmosis composite membrane first went up then remained stable: when the incorporation concentration was 0.01 wt%, the prepared forward osmosis composite membrane was reversed. The solute flux was 2.94 g m⁻² h⁻¹ (FO mode) and 4.02 g m⁻² h⁻¹ (PRO mode); when the incorporation concentration was 0.05 wt%, the reverse solute flux increased to 3.24 g m⁻² h⁻¹ (FO mode) and 4.78 g m⁻² h⁻¹ (PRO mode); when the incorporation concentration was 0.1 wt%, the reverse solute flux continued increase to 5.13 g m⁻² h⁻¹ (FO mode) and 9.05 g m⁻² h⁻¹ (PRO mode); when the incorporation concentration was 0.3 wt%, the reverse solute flux was 5.18 g m⁻² h⁻¹ (FO mode) and 9.27 g m⁻² h⁻¹ (PRO mode). It can be seen that the reverse solute flux peaks when the incorporation concentration was 0.1 wt%. According to the morphological and chemical structure analysis of the previous article, when the incorporation concentration was low (0.01 wt%), the nano-TiO₂ particles on the surface of the forward osmosis membrane have little influence on the structure of the active layer, and the size of the reverse solute flux and the unmodified membranes are similar; when the incorporation concentration was increased (0.05 wt%, 0.1 wt%), the nano-TiO₂ particles in the active layer of the modified forward osmosis composite membrane promote the

formation of the polyamide layer, and the degree of cross-linking was higher than that without the modified membrane. However, at the same time, it can be seen from the electron microscopy image that nanochannels were formed on the surface of the polyamide layer, which provided conditions for the salt to pass through thus the reverse solute flux of the membrane increased simultaneously; However, when the incorporation concentration was too large (0.3 wt%), the polymerization of the incorporated nano-TiO₂ particles disrupts the structure of the polyamide layer, the degree of cross-linking was greatly reduced, and there were obvious nano-channels on the surface of the membrane active layer, as a result, the reverse solute flux of the membrane continues to increase.

4. Conclusions

This paper investigated the optimal incorporation concentration of nano-TiO₂ particles prepared by in-situ incorporated modified forward osmosis composite membranes. By examining the surface morphology, chemical structure, and permeability of the membrane support layer and active layer, the following conclusions were obtained: (1) With the increase of the concentration of nano-TiO₂ particles during in-situ incorporation in water bath, the nanoparticles presented on the surface and internal voids of the polysulfone support layer also increased, the dispersion of the nanoparticles on the membrane surface increased, but when the incorporated concentration was too large, the nanoparticles aggregated and caused pore blocking in the pore structure. (2) With the increase of the concentration of TiO₂ incorporated in situ process, the water flux showed a trend of rising first and then decreased, and the reverse solute flux showed an upward trend. The optimal concentration of nano-TiO₂ particles for in-situ incorporation was 0.1 wt % due to its high membrane permeability and low internal concentration polarization.

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