

Effects of Substrate on Interfacial Polymerization: Tuning the Hydrophobicity via Polyelectrolyte Deposition

Xin Liu¹, Ge Liu¹, Weiyi Li², Qinyu Wang¹, and Baolin Deng¹

¹Affiliation not available

²Southern University of Science and Technology

May 8, 2020

Abstract

Interfacial polymerization (IP) has been the key method for fabricating thin film composite (TFC) membranes. However, the role of the substrate surface hydrophilicity in the IP-film formation remains a controversial issue to be further addressed. This study characterized the IP films formed on a series of polyacrylonitrile (PAN) substrates whose hydrophilicity were varied via different approaches, including the alkaline treatment and the deposition of various polycations. It was revealed that delamination could occur when the IP film was formed on a relatively hydrophilic surface; the integrity of the TFC membranes was substantially improved owing to the modification of polyelectrolyte deposition. On the other hand, the characterization indicated that the TFC membrane could have an enhanced efficiency when the substrate was relatively hydrophilic. It is established that the polyelectrolyte deposition can be exploited to effectively tune the substrate surface hydrophobicity, thereby increasing the degrees of freedom for optimizing TFC membranes fabrication.

Introduction

Thin film composite (TFC) membranes are essential for various membrane-based applications, such as seawater desalination, ultrapure water production and advanced wastewater treatment^{1,2}, which play an important role in the sustainable development of economy and society. The superior performance of TFC membranes could be attributed to the ultrathin selective layer that is mainly formed via interfacial polymerization (IP). Numerous endeavors have been devoted to optimizing the IP process to improve the permeability and selectivity of a TFC membrane^{3,4}. Despite the increase in studies focusing on fabricating TFC membranes^{3,5}, limited knowledge is available about the mechanisms accounting for the formation of an IP film.

Most prior studies investigated the selective layer (i.e., the polyamide layer) and support layer (i.e., the substrate) of a TFC membrane separately^{6,7} and the focus was usually on the optimization of the selective layer. There are a limited number of studies that explored the effects of the substrate on the formation of a polyamide (PA) layer. It has been recognized that both the pore-size distribution and surface hydrophilicity of the substrate are two of the most important factors affecting the formation of a PA layer⁸. Singh *et al.*⁹ explored the effects of substrate structures on the PA-layer formation by employing two polysulfone substrates with varied pore-size distributions. It was revealed that increasing the pore size could lead to a relatively thin PA layer with a higher permeability. Similar observations were obtained by Ghosh and Hoek in a later study⁸. In addition to varying the pore size, the effects of the morphology were highlighted in the work by ElSherbiny *et al.*¹⁰, where a novel polyethersulfone substrate with isotropic pores (~100 nm) was developed by combining the vapor- and nonsolvent-induced phase separation; this novel substrate yielded a TFC membrane with a higher water permeability compared with those fabricated using commercial substrates, while maintaining the salt rejection. In comparison with the studies on the effects of

substrate structures, there are substantially different opinions in the open literature interpreting the role of the hydrophilicity of the substrate in an IP process.

The preference of a hydrophobic substrate for IP was supported by prior studies in different ways. For example, Ghosh and Hoek⁸ proposed a conceptual model suggesting that a relatively hydrophobic substrate would result in a highly permeable TFC membrane. Specifically, it was hypothesized that enhancing the hydrophilicity of the substrate could impede the diffusion of m-phenylenediamine (MPD) in the aqueous phase while promoting the diffusion of trimesoyl chloride (TMC) in the organic phase into the substrate pores to form a thicker PA layer during IP. In contrast, the work by Alsvik *et al.*¹¹ highlighted the delamination phenomenon of a PA layer formed on a hydrophilic substrate of hydrolyzed cellulose acetate (CA). In order to improve the adhesion between the PA layer and the hydrophilic substrate, they proposed to precoat the substrate with a TMC-containing solution taking advantage of the hydroxyl groups on the CA network; this TMC-precoated substrate would allow the covalent bonding with the PA layer and the hydrophilic substrate. Delamination of the active layer was also observed by Zhang *et al.*¹² when using a series of polysulfone (PSf) substrates for fabricating the TFC membranes via IP, though the underlying mechanism remained unclear.

On the contrary, there are prior studies indicating that increasing the hydrophilicity of the substrate could not only enable the membrane-supported IP but also improve the performance of the resulting TFC membrane. For example, Kim *et al.*¹³ demonstrated that a plasma treatment would allow polypropylene (PP) and PSf membranes to be used as the substrate for IP owing to the increase in the hydrophilicity. A similar method was adopted by Kim *et al.*¹⁴ to successfully fabricate a TFC membrane via IP using a hydrophobic polyvinylidene fluoride (PVDF) substrate. In addition to the plasma treatment, it was reported that the hydrophilicity of the substrate could be enhanced by surface coating and incorporating hydrophilic additives in the dope solutions so as to favor the formation of a PA layer via membrane-supported IP and improve the TFC membrane performance. For instance, Jimenez-Solomon *et al.*¹⁵ successfully fabricated TFC membranes via IP using crosslinked polyimide and poly(ether ether ketone) substrates, whose hydrophilicity was increased by simply dipping the substrates into a solution of polyethylene glycol before the IP; Ding *et al.*¹⁶ examined the effects of substrate hydrophilicity on the performance of the TFC membranes fabricated via IP by varying the amount of polyvinylpyrrolidone mixed into the PSf dope solutions, which were used to prepare the substrates via phase inversion.

Despite the discrepancy between the studies on the role of substrate hydrophilicity in the formation of a PA layer via membrane-supported IP, it has been widely accepted that a hydrophilic substrate would substantially improve the performance of a TFC membrane employed in an osmotically driven process owing to the mitigation of the internal concentration polymerization (ICP) and fouling¹⁷. Although the potential of applying osmotically driven membrane processes to desalination remains controversial^{18,19}, great promise has been shown in their applications for pharmaceutical production²⁰, food and beverage industry²¹, emergent relief²², wastewater treatment²³, and energy generation²⁴. Therefore, it is of great significance to develop TFC membranes with a hydrophilic substrate for various osmotically driven membrane processes.

A limited number of studies were reported to develop an effective method for synthesizing TFC membranes with a hydrophilic substrate. In addition to the method based on the TMC precoating by Alsvik *et al.*¹¹, Choi *et al.*²⁵ successfully fabricated a nanoscale-controlled PA layer with a typical thickness ~15 nm by depositing the complementary monomers (i.e., MPD and TMC) alternately on a polyelectrolyte-modified hydrophilic polyacrylonitrile (PAN) substrate; Park *et al.*²⁶ employed toluene/xylene as the solvent for the organic phase and synthesized TFC membranes with higher performance for reverse osmosis (RO) using a hydrophilic PAN membrane as the substrate; the method developed by Park *et al.*²⁶ was further optimized by Kwon *et al.*²⁷ and the synthesized TFC membranes were examined in a forward osmosis (FO) process. However, most of these studies ignored the effects of substrate hydrophilicity on the formation of the PA layer.

Instead of targeting on the fabrication of TFC membrane with superior performance, the focus of the current study was on the role of substrate hydrophilicity in a membrane-supported IP process. In line with this idea, the formation of a PA layer via membrane-supported IP was investigated when varying the hydrophilicity

of the substrate. Particularly, it was proposed to tune the surface hydrophilicity of the substrate via the deposition of various polyelectrolytes, which have been extensively explored for the Layer-by-Layer (LbL) assembly^{28,29}. The relative importance of the enhanced surface hydrophobicity in the IP-film formation was analyzed in terms of a series of characterization experiments. It was confirmed that the polyelectrolyte deposition could increase the surface hydrophobicity of a hydrolyzed PAN substrate and thereby favor the formation of an IP layer with better integrity (i.e., minimized delamination). The performance of the fabricated TFC membranes with the hydrolyzed PAN substrate was evaluated in an FO process to verify the mitigation of the ICP by the hydrophilic substrate.

Experimental Procedures

Interfacial polymerization on substrates with varied hydrophilicity

The substrates employed for the membrane-supported IP in this study were all fabricated using polyacrylonitrile (PAN) via phase inversion, whose various applications were reported in our previous publications³⁰⁻³². Specifically, the dope solution was prepared by dissolving polymer particles of PAN (weight-averaged molecular weight $M_w \sim 150,000$, Sigma-Aldrich) in N,N-dimethylformamide (DMF, [?] 99.8% , Alfa Aesar) with a predetermined amount of lithium chloride (LiCl, [?] 99% , Sigma-Aldrich) as the pore former^{31,32}. The mass ratio of PAN, LiCl, and DMF in the dope solution was 18:2:80. The dope solution was mixed using a magnetic stirrer (IKA, C-MAG HS7 Control, Germany) at a temperature of $\sim 60^\circ\text{C}$. The film-coated glass plate (casting height $\sim 150\ \mu\text{m}$) was immediately immersed into a coagulation bath of tap water at room temperature ($\sim 20^\circ\text{C}$) to initiate the nonsolvent-induced phase inversion. The unmodified PAN films were denoted as PAN-O and used as the substrates in the control tests.

The hydrophilicity of the PAN-O films was first changed by implementing an alkaline treatment, whereby the nitrile groups would be converted into carboxyl groups³³. Specifically, the PAN-O films were soaked into a 1.5 M NaOH ([?] 96% , Fuchen Chemical, China) solution at 45°C for 90 min^{31,32}. The resulting PAN substrates were designated as PAN-A. In order to isolate the effects resulting from the pore-size change³⁴, a comparative study was carried out by applying a heat treatment to the PAN-O films. Specifically, the PAN-O substrates were immersed in a bath of Milli-Q water while the temperature and duration were kept at the same values for the alkaline treatment (i.e., 45°C for 90 min). The resulting PAN substrates were denoted as PAN-H.

The membrane-supported IP was performed by impregnating the PAN substrates with an aqueous solution containing 2.0 wt.% *m*-phenylenediamine (MPD, [?] 99% , Sigma-Aldrich) and exposing the impregnated PAN substrates to an organic solution containing 0.1 w/v.% 1,3,5-benzenetricarbonyl trichloride (TMC, [?] 99% , Sigma-Aldrich). In particular, the solvent of the TMC-containing organic solution was hexane ([?] 98% , Shanghai Aladdin Biochemical Technology Co. Ltd., China); the duration for soaking the PAN substrates in the MPD-containing aqueous solution was approximately 5 min and the excessive MPD solution was removed using an air knife of compressed N_2 ; the duration for exposing the impregnated PAN substrates to the TMC-containing organic solution was approximately 1 min and the residual TMC was removed by a rinse of pure hexane.

Tuning the hydrophilicity of substrates via polyelectrolyte deposition

The PAN-A substrates enabled the surface modification via the deposition of polycations owing to the negatively charged surface after the alkaline treatment (i.e., the formation of carboxyl groups). It was expected that the deposition of various polycations would significantly alter the hydrophilicity of the PAN-A substrates^{28,35}. Particularly, three polycations were employed to modify the PAN-A substrates, including poly(allylamine hydrochloride) (PAH, $M_w \sim 120,000$ to $200,000$, [?] 99% , Alfa Aesar), polyethyleneimine (PEI, $M_w \sim 750,000$, 50%, Sigma-Aldrich), and poly(dimethyl diallyl ammonium chloride) (PDADMAC, $M_w \sim 200,000$ to $350,000$, 20%, Sigma-Aldrich). The deposition of the polycations on the PAN-A substrates was implemented in a way similar to that employed by the Layer-by-Layer assembly using polyelectrolytes^{31,32}. Specifically, 1 g of the polycation was dissolved in 1 L Milli-Q water containing 0.5 M sodium chloride (NaCl, [?] 99.5% , Xilong Scientific, China); the existence of NaCl would favor the assembly of the polyelectrolyte

on the surface of the substrate³⁶. The PAN-A substrate was placed in a stainless steel plate with the dense side facing up. A predetermined amount of the polycation solution was gently poured into the plates to contact with the surface of the PAN-A substrate. The duration of exposing the PAN-A substrate to the polycation solution was 20 min and the deposition was followed by a 10 min rinse of Milli-Q water to remove the excess polyelectrolyte on the substrate. The polyelectrolyte-modified substrates were denominated as XXX-m, where XXX indicates the specific polyelectrolyte used for the substrate modification. All the polyelectrolyte-modified substrates are summarized in Table S-1.

Membrane characterization

The hydrophilicity of the PAN substrates was characterized in terms of the contact angle measurement. All the PAN substrates were dried using a freeze dryer (Ningbo Scientz Biotechnology Co. Ltd., Scientz-12N, China) before the contact angle measurement and the sessile drop method was employed using a Drop Shape Analyzer (KRUSS GmbH, DSA25, Germany). The measurement was repeated (at least 9 times using three independently prepared membrane samples) to obtain an averaged value for a more accurate analysis.

It has been revealed in prior studies³⁷ that surface morphology could play an important role in the surface wetting. Therefore, both scanning electron microscopy (SEM) and atomic force microscopy (AFM) were exploited to characterize the surface of the PAN substrates. In particular, the SEM characterization was performed by precoating the membrane samples with platinum in a vacuum electric sputter coater (Quorum, Q150TES, UK) and then observing the precoated samples on a SEM system (ZEISS, MerlinTM, Germany). The surface roughness of the PAN substrates was analyzed using an AFM system (Asylum Research, MFP-3DTM Stand Alone, USA) associated with Asylum Research.

The TFC membranes were characterized using an osmotically driven process, whereby the efficiency of FO was estimated to assess the effect of the substrate on the ICP. Specifically, the water permeability (A) of the membrane was measured using a high pressure crossflow-filtration setup (Fumei Filter & Membrane Technology, FlowMem0021-HP, China). The osmotically driven process was performed by employing a 2 M NaCl solution as the draw solution (DS) and the water flux was measured by weighing the feed solution (i.e., pure water). The efficiency of FO (η_{FO}) then was calculated as the ratio of the measured flux to the ideal one (i.e., the product of the water permeability and the osmotic pressure difference). In addition, the salt rejection (R) of the TFC membrane was determined in terms of the conductivity measurement with a 20 mM NaCl solution as the feed. All the measurements were repeated at least three times to obtain the averaged values for a more accurate analysis.

Results and discussion

Effects of substrate hydrophilicity on the IP-film formation

The measurement results in Figure 1 indicate that the PAN-O membrane yielded a contact angle of approximately 67° , confirming the relatively high hydrophilicity of PAN for fabricating TFC membranes via IP³⁸. The negligible difference in the contact angle between the PAN-O and PAN-H membranes indicates that the heat treatment with a temperature of 45°C had little impact on the hydrophilicity of the PAN substrate. In contrast, the introduction of carboxyl groups by the alkaline treatment markedly increased the hydrophilicity of the PAN substrate as indicated by the decrease in the contact angle for the PAN-A membrane in Figure 1.

Hosted file

image1.emf available at <https://authorea.com/users/319831/articles/449525-effects-of-substrate-on-interfacial-polymerization-tuning-the-hydrophobicity-via-polyelectrolyte-deposition>

The SEM images in the upper panel of Figure S-1a exhibit the dense side of the three PAN substrates. It can be observed that there exist nano-sized pores on the surface of both the PAN-O and PAN-H substrates, though the sizes of the pores on the surface of the PAN-H substrate are substantially smaller than those on

the surface of the PAN-O substrate. On the other hand, there are no discernable pores in the SEM image for the surface of the PAN-A substrate. All these observations indicate that the PAN polymer network was shrunk owing to the stress relaxation of PAN polymer in the water bath at an elevated temperature of 45°C³¹; the swelling of PAN polymer network resulting from the alkaline treatment further reduced the pore size³⁹. The cross-sectional SEM images shown in the lower panel of Figure S-1a confirms that the heat and alkaline treatments could have marginal effects on the figure-like macrovoids beneath the dense skin.

The representative AFM images in Figure S-1b indicate that all the PAN substrates have similar values of the roughness in terms of the root mean square (RMS); the RMS roughness values for the PAN-O and PAN-H substrates are nearly the same (approximately 2.4±0.2 nm), while that of the PAN-A substrate is increased to 3.2±0.2 nm. This supports the assumption that the geometrical changes resulting from the post-treatments could be ignored when analyzing the effects of the substrate on the IP process.

The water permeabilities of all the PAN substrates were evaluated in terms of the flux-transmembrane pressure (TMP) relationship and the evaluation results are compared in Figure 2. It is evident that both the heat and alkaline treatments substantially increased the hydraulic resistance of the substrate. In particular, the hydrolysis in the NaOH solution resulted in an even lower value of the water permeability (82.2±3.9 LMH/bar) when compared with that for the PAN-H substrate (113.0±2.6 LMH/bar). These observations are consistent with the changes in the surface pore sizes on the dense side as revealed by the SEM images in Figure S-1a.

Hosted file

image2.emf available at <https://authorea.com/users/319831/articles/449525-effects-of-substrate-on-interfacial-polymerization-tuning-the-hydrophobicity-via-polyelectrolyte-deposition>

TFC membranes fabricated using the PAN-O, PAN-H, and PAN-A substrates via IP were characterized by SEM; the SEM images of the top view with varied scales and cross-sectional view are demonstrated in Figures 3a and 3b, respectively. The upper panel of Figures 3a shows the top views at a lower magnification. It evidently indicates that the IP film was not firmly ‘locked’ by the surface of the PAN-A substrate and irregularly split into smaller pieces with curved or folded edges. In contrast, both the PAN-O and PAN-H substrates yielded a relatively uniform and ‘undamaged’ IP layer, whose typical ridge and valley substructures^{3,40} are resolved by zooming in on the surface of the IP layer (the lower panel of Figures 3a). The SEM image with a higher magnification also reveals similar substructures of the IP layer peeling off from the PAN-A substrate.

Hosted file

image3.emf available at <https://authorea.com/users/319831/articles/449525-effects-of-substrate-on-interfacial-polymerization-tuning-the-hydrophobicity-via-polyelectrolyte-deposition>

The cross-sectional views in Figures 3b provide further evidence for the delamination of the TFC membrane fabricated using the PAN-A substrate. These observations are consistent with the work by Alsvik *et al*.¹¹, arguing that the hydrophilicity of the substrate could result in unfavorable interactions between the generated IP layer and substrate. It is also interesting to note that the PAN-H substrate yielded an IP layer with thicker substructures (~500 nm) in comparison with those (~300 nm) resulting from the PAN-O substrate. The shrinkage of the surface pores might increase the resistance for the diffusion of MPD in the aqueous phase and thereby favor the development of the polymerization toward the aqueous phase, which is similar to the case of a lower concentration of MPD (i.e., limited diffusion on the aqueous side) in the work by Chai and Krantz⁴¹. When the evolution of the coupled diffusion and reaction processes was spatially dominated by the porous surface of the substrate, it was reasonable to expect that the polymerization should be perturbed in a destabilizing way to yield more periodic patterns, such as the extended ‘leaves’⁴⁰.

The experimental results for the water permeability and salt rejection of NaCl are displayed in Figures 4a and 4b, respectively. The integrity of the IP layers formed on the PAN-O and PAN-H substrates is confirmed

by comparing the water permeability for the TFC membranes with different PAN substrates; that is, the water permeabilities for the TFC-O and TFC-H are significantly decreased, whereas the one for the TFC-A is almost equal to that for the substrate as shown in Figure 2. On the other hand, it is not surprising to note that the salt rejection of NaCl for the TFC membrane with the PAN-A substrate is much lower than those for the TFC membranes with the PAN-O and PAN-H substrates, since the active layer peeled off on the surface of the PAN-A substrate. Moreover, the TFC-H has a lower water permeability compared with that for the TFC-O substrate, whereas the corresponding rejection of NaCl is slightly increased. This is consistent with the SEM characterization showing an IP layer with thicker substructures for the TFC membrane with the PAN-H substrate, thereby offering additional evidence for the integrity of the TFC-O and TFC-H.

Hosted file

image4.emf available at <https://authorea.com/users/319831/articles/449525-effects-of-substrate-on-interfacial-polymerization-tuning-the-hydrophobicity-via-polyelectrolyte-deposition>

Effects of the polyelectrolyte deposition on the IP-film formation

It has been demonstrated that increasing the hydrophilicity of the substrate could result in the delamination of the TFC membrane fabricated via IP. However, it was tempting to employ a hydrophilic substrate for fabricating a TFC membrane via IP owing to the potential advantages for improving the efficiency during an FO process. Therefore, the polyelectrolyte deposition was exploited to modify the surface wettability. Three polycations, including PDADMAC, PEI, and PAH, were employed to tune the surface of the PAN-A substrate (schematically shown in Figure S2), which was negatively charged owing to the carboxyl groups.

The contact-angle measurement results for the polyelectrolyte-modified PAN-A substrates are shown and compared in Figure 5. In particular, the red dashed line denotes the average contact angle for the PAN-A substrate, while the gray dashed line is for the PAN-O substrate. It clearly indicates that the deposition of all the polycations significantly decreased the degree of the surface hydrophilicity for the PAN-A substrate. The PAN-A substrate modified by PDCDMAC yielded the smallest contact angle, which was greater than that for the unmodified PAN-A substrate. On the other hand, the degrees of the surface hydrophobicity for the PAN-A substrates modified by PEI and PAH were even higher than that for the PAN-O substrate. Especially, the PAN-A substrate modified by PAH yielded the largest contact angle greater than 90°. Moreover, the substantial increase in the surface hydrophobicity indicates that most of the nonpolar segments should be exposed to the liquid phase while ‘preventing’ the polar groups (i.e., the amine groups) from meeting with the TMC in the organic phase. It is reasonable to assume that the effects of the functional groups introduced by the polyelectrolytes could be ignored to focus on the variation in the hydrophobicity.

Hosted file

image5.emf available at <https://authorea.com/users/319831/articles/449525-effects-of-substrate-on-interfacial-polymerization-tuning-the-hydrophobicity-via-polyelectrolyte-deposition>

In terms of the SEM images in Figures S-2a, the polyelectrolyte deposition further ‘removed’ the pore structures, which are discernable in the SEM image for the PAN-O substrate in Figure S-1a. All the polyelectrolyte-modified PAN-A substrates yielded an RMS value of roughness ~ 3.5 nm (Figure S-2a), which was slightly higher than that for the unmodified PAN-A substrate (~ 3.2 nm) as demonstrated in Figure S-1b. Despite the marginal difference in the geometrical characteristics, it is interesting to note that the PAN-A substrate modified by PAH gave rise to a slightly high value of the surface roughness; this is consistent with the observation in prior studies⁴² that relatively high heterogeneity could result from the deposition of PAH.

Hosted file

image6.emf available at <https://authorea.com/users/319831/articles/449525-effects-of-substrate-on-interfacial-polymerization-tuning-the-hydrophobicity-via-polyelectrolyte-deposition>

deposition

The characterization results in Figure 6 affirms that the deposition of all the polycations significantly increased the hydraulic resistance of the PAN-A substrate, even though the deposited layer should have a negligible thickness of a few nanometers²⁹. Moreover, the variation in the water permeability is consistent with the varying wettability characterized by their contact angles in Figure 5. That is, the relatively hydrophilic surface of the PAN-A substrate modified by PDADMAC yielded the highest water permeability, whereas the lowest water permeability corresponded to the hydrophobic surface resulting from the deposition of PAH.

Hosted file

image7.emf available at <https://authorea.com/users/319831/articles/449525-effects-of-substrate-on-interfacial-polymerization-tuning-the-hydrophobicity-via-polyelectrolyte-deposition>

A series of TFC membranes were fabricated using the polyelectrolyte-modified PAN-A substrates and characterized by SEM to generate the top views with varied magnifications and cross-sectional views in Figures 7a and 7b, respectively. It is evident that delamination occurred during the IP for fabricating the TFC-A and TFC-PDADMAC. This observation is consistent with the hypothesis that a surface more hydrophilic than that of the PAN-O substrate could be unfavorable for ‘locking’ the generated IP layer; the water wettability of the surface modified by PDADMAC was slightly higher than that of the PAN-O substrate, though the deposition of PDADMAC somehow increased the hydrophobicity of the surface of the PAN-A substrate as revealed by the contact-angle characterization in Figure 5.

All the IP layers generated on the polyelectrolyte-modified PAN-A substrates were characteristic of relatively dense and smooth substructures in terms of the top views at a larger magnification. A possible explanation is that the relatively hydrophobic surface could favor the diffusion of TMC in the organic phase toward the interface of polymerization and thereby enhance the degree of crosslinking⁴³, which might limit the growth of heterogeneous substructures. On the other hand, the cross-sectional views indicate that thinner IP layers (~200 nm) were formed on the surface of the PAN-A substrates modified by PEI and PAH. This observation is consistent with the hypothesis that the film formation should be dominated by the crosslinking that yielded a relatively dense network and accelerated the IP process toward the self-limiting regime⁴⁴. In addition, the cross-sectional view for the TFC-A and TFC-PDADMAC verifies the IP-layer detachment from the substrate.

The integrity of the TFC-PEI and TFC-PAH is confirmed by the characterization results of the water permeability and NaCl rejection, which are displayed in Figures 8a and 8b, respectively. Although the TFC-PAH yielded a lower value of the water permeability compared with that for the TFC-PEI, it achieved the highest rejection of NaCl with a value of ~90%. Having a higher value of water permeability and a lower value of NaCl rejection just manifest the imperfect IP layer formed on the PAN-A substrate modified by PDADMAC. The characterization results also imply that less part of the IP layer peeled off from the surface modified by PDADMAC, since the water permeability is markedly lower than that for the PAN-A substrate.

Hosted file

image8.emf available at <https://authorea.com/users/319831/articles/449525-effects-of-substrate-on-interfacial-polymerization-tuning-the-hydrophobicity-via-polyelectrolyte-deposition>

In order to clarify if the employment of a hydrophilic substrate would offer any advantages over the relatively hydrophobic substrate, both the TFC membranes with the PAN-O substrate and the PAN-A substrate modified by PAH were further characterized using FO processes. The water flux was measured employing two different membrane orientations; that is, the active layer was exposed to the draw solution (AL-DS) or the feed solution (AL-FS). Despite the orientation difference (i.e., different degree of ICP^{45,46}), the TFC-PAH yielded a water flux of ~26 LMH, which was nearly twofold greater than the water flux of ~13 LMH for the TFC-O as shown in Figure 9a. Therefore, it is reasonable to infer that the wettability of the substrate network

could have substantial impact on the ICP. The calculation results of FO efficiency are shown and compared in Figure 9b. It is evident that the FO efficiency of the TFC-PAH was almost doubled compared with that for the TFC-O. However, it is quite challenging to unravel the mechanisms accounting for the complex transport phenomena in the substrate, especially when the effects of the wettability of the polymeric network cannot be ignored. A possible explanation is that the variation in the wettability could significantly change the topological substructures of the network^{47,48} and thereby give rise to different paths effective for the fluid flow and the solute flux.

Hosted file

image9.emf available at <https://authorea.com/users/319831/articles/449525-effects-of-substrate-on-interfacial-polymerization-tuning-the-hydrophobicity-via-polyelectrolyte-deposition>

Conclusions

The effects of the PAN substrate on the IP-film formation were investigated while highlighting the role of the surface hydrophilicity. The hydrophilicity of the PAN substrate was first modified by implementing the alkaline treatment and characterized by the contact-angle measurement. The surface of the PAN substrate modified by the alkaline treatment was further tuned by the deposition of different polyelectrolytes to vary the degree of hydrophilicity. All the modified PAN substrates were employed to fabricate the TFC membranes via IP and the formed IP layers were compared to correlate the film formation with the degree of hydrophilicity. The following conclusions can be drawn from the characterization results:

1. The PAN substrate with a relatively hydrophilic surface could result in delamination when employed to fabricate the TFC membrane via IP, whereas the integrity of the IP layer can be improved by decreasing the surface hydrophilicity.
2. The deposition of various polycations onto the surface of the PAN substrate can change the wettability to different degrees, thereby offering a tool for the IP-based fabrication of TFC membranes with a hydrophilic PAN substrate.
3. The comparative study of evaluating the TFC membranes with different PAN substrates indicated that a relatively hydrophilic substrate would favor the enhancement of the water-flux efficiency when employed in an FO process.

All the modified PAN substrates were also examined by SEM and AFM; the characterization results confirmed that the variations in the geometrical characteristics were negligible. Therefore, it is reasonable to believe that the effects of the modified PAN substrates on the IP-film formation were primarily attributed to the changes in the surface wettability. The application of polyelectrolyte deposition not only provided an approach to investigating the effects of the surface hydrophilicity, but also opened new paradigm for optimizing the fabrication of TFC membranes via IP.

Acknowledgments

This study is supported by National Natural Science Foundation of China (Grant No. 21878140), the Program for Guangdong Introducing Innovative and Entrepreneurial Teams (Grant No. 2017ZT07Z479), and the Shenzhen Science and Technology Innovation Committee (Grant No. JCYJ20190809172011680). The authors are also grateful to the support of the Centers for Mechanical Engineering Research and Education at MIT and SUSTech. The SEM data were obtained using the equipment maintained by Southern University of Science and Technology Core Research Facilities (CRF).

References

1. Misdan N, Lau WJ, Ismail AF. Seawater Reverse Osmosis (SWRO) desalination by thin-film composite membrane-Current development, challenges and future prospects. *Desalination*. 2012;287:228-237.
2. Yip NY, Tiraferri A, Phillip WA, Schiffman JD, Elimelech M. High performance thin-film composite forward osmosis membrane. *Environmental Science and Technology*. 2010;44(10):3812-3818.

3. Yang Z, Guo H, Tang CY. The upper bound of thin-film composite (TFC) polyamide membranes for desalination. *Journal of Membrane Science*. 2019;590.
4. Cadotte JE, Petersen RJ, Larson RE, Erickson EE. A new thin-film composite seawater reverse osmosis membrane. *Desalination*. 1980;32:25-31.
5. Ismail AF, Padaki M, Hilal N, Matsuura T, Lau WJ. Thin film composite membrane - Recent development and future potential. *Desalination*. 2015;356:140-148.
6. Li X, Li Q, Fang W, Wang R, Krantz WB. Effects of the support on the characteristics and permselectivity of thin film composite membranes. *Journal of Membrane Science*. 2019;580:12-23.
7. Rao AP, Joshi SV, Trivedi JJ, Devmurari CV, Shah VJ. Structure-performance correlation of polyamide thin film composite membranes: Effect of coating conditions on film formation. *Journal of Membrane Science*. 2003;211(1):13-24.
8. Ghosh AK, Hoek EMV. Impacts of support membrane structure and chemistry on polyamide-polysulfone interfacial composite membranes. *Journal of Membrane Science*. Jul 2009;336(1-2):140-148.
9. Singh PS, Joshi SV, Trivedi JJ, Devmurari CV, Rao AP, Ghosh PK. Probing the structural variations of thin film composite RO membranes obtained by coating polyamide over polysulfone membranes of different pore dimensions. *Journal of Membrane Science*. 2006;278(1-2):19-25.
10. ElSherbiny IMA, Ghannam R, Khalil ASG, Ulbricht M. Isotropic macroporous polyethersulfone membranes as competitive supports for high performance polyamide desalination membranes. *Journal of Membrane Science*. 2015;493:782-793.
11. Alsvik IL, Hagg MB. Preparation of thin film composite membranes with polyamide film on hydrophilic supports. *Journal of Membrane Science*. Feb 2013;428:225-231.
12. Zhang Q, Zhang Z, Dai L, Wang H, Li S, Zhang S. Novel insights into the interplay between support and active layer in the thin film composite polyamide membranes. *Journal of Membrane Science*. 2017;537:372-383.
13. Kim HI, Kim SS. Plasma treatment of polypropylene and polysulfone supports for thin film composite reverse osmosis membrane. *Journal of Membrane Science*. 2006;286(1-2):193-201.
14. Kim ES, Kim YJ, Yu Q, Deng B. Preparation and characterization of polyamide thin-film composite (TFC) membranes on plasma-modified polyvinylidene fluoride (PVDF). *Journal of Membrane Science*. 2009;344(1-2):71-81.
15. Jimenez-Solomon MF, Gorgojo P, Munoz-Ibanez M, Livingston AG. Beneath the surface: Influence of supports on thin film composite membranes by interfacial polymerization for organic solvent nanofiltration. *Journal of Membrane Science*. 2013;448:102-113.
16. Ding C, Yin J, Deng B. Effects of Polysulfone (PSf) Support Layer on the Performance of Thin-Film Composite (TFC) Membranes. *Journal of Chemical and Process Engineering*. 08/02 2013;1.
17. McCutcheon JR, Elimelech M. Influence of membrane support layer hydrophobicity on water flux in osmotically driven membrane processes. *Journal of Membrane Science*. 2008;318(1-2):458-466.
18. Wang YN, Goh K, Li X, Setiawan L, Wang R. Membranes and processes for forward osmosis-based desalination: Recent advances and future prospects. *Desalination*. 2018;434:81-99.
19. McCutcheon JR. Avoiding the Hype in Developing Commercially Viable Desalination Technologies. *Joule*. 2019;3(5):1168-1171.
20. Lay WCL, Zhang Q, Zhang J, et al. Effect of Pharmaceuticals on the Performance of a Novel Osmotic Membrane Bioreactor (OMBR). *Separation Science and Technology*. 2012;47(4):543-554.

- 21.** Garcia-Castello EM, McCutcheon JR. Dewatering press liquor derived from orange production by forward osmosis. *Journal of Membrane Science*. 2011;372(1-2):97-101.
- 22.** Cath TY, Childress AE, Elimelech M. Forward osmosis: Principles, applications, and recent developments. *Journal of Membrane Science*. 2006;281(1):70-87.
- 23.** Zhao S, Zou L, Tang CY, Mulcahy D. Recent developments in forward osmosis: Opportunities and challenges. *Journal of Membrane Science*. 2012;396:1-21.
- 24.** Logan BE, Elimelech M. Membrane-based processes for sustainable power generation using water. *Nature*. 2012;488(7411):313-319.
- 25.** Choi W, Jeon S, Kwon SJ, et al. Thin film composite reverse osmosis membranes prepared via layered interfacial polymerization. *Journal of Membrane Science*. Apr 2017;527:121-128.
- 26.** Park SJ, Kwon SJ, Kwon HE, et al. Aromatic solvent-assisted interfacial polymerization to prepare high performance thin film composite reverse osmosis membranes based on hydrophilic supports. *Polymer*. 2018;144:159-167.
- 27.** Kwon HE, Kwon SJ, Park SJ, et al. High performance polyacrylonitrile-supported forward osmosis membranes prepared via aromatic solvent-based interfacial polymerization. *Separation and Purification Technology*. 2019;212:449-457.
- 28.** Ishigami T, Amano K, Fujii A, et al. Fouling reduction of reverse osmosis membrane by surface modification via layer-by-layer assembly. *Separation and Purification Technology*. 2012;99:1-7.
- 29.** Xu G-R, Wang S-H, Zhao H-L, et al. Layer-by-layer (LBL) assembly technology as promising strategy for tailoring pressure-driven desalination membranes. *Journal of Membrane Science*. 2015;493:428-443.
- 30.** Qi S, Li Y, Zhao Y, Li W, Tang CY. Highly Efficient Forward Osmosis Based on Porous Membranes—Applications and Implications. *Environmental Science & Technology*. 2015;49(7):4690-4695.
- 31.** Liu X, Qi S, Li Y, Yang L, Cao B, Tang CY. Synthesis and characterization of novel antibacterial silver nanocomposite nanofiltration and forward osmosis membranes based on layer-by-layer assembly. *Water Research*. 2013;47(9):3081-3092.
- 32.** Liu X, Foo LX, Li Y, Lee JY, Cao B, Tang CY. Fabrication and characterization of nanocomposite pressure retarded osmosis (PRO) membranes with excellent anti-biofouling property and enhanced water permeability. *Desalination*. 2016;389:137-148.
- 33.** Wang ZG, Wan LS, Xu ZK. Surface engineering of polyacrylonitrile-based asymmetric membranes towards biomedical applications: An overview. *Journal of Membrane Science*. 2007;304(1-2):8-23.
- 34.** Strathmann H, Kock K. The formation mechanism of phase inversion membranes. *Desalination*. 1977;21(3):241-255.
- 35.** Suwaileh W, Johnson D, Khodabakhshi S, Hilal N. Development of forward osmosis membranes modified by cross-linked layer by layer assembly for brackish water desalination. *Journal of Membrane Science*. 2019;583:267-277.
- 36.** Duong PHH, Zuo J, Chung TS. Highly crosslinked layer-by-layer polyelectrolyte FO membranes: Understanding effects of salt concentration and deposition time on FO performance. *Journal of Membrane Science*. 2013;427:411-421.
- 37.** Shimanovich DL, Vorobjova AI, Tishkevich DI, Trukhanov AV, Zdorovets MV, Kozlovskiy AL. Preparation and morphology-dependent wettability of porous alumina membranes. *Beilstein Journal of Nanotechnology*. 2018;9:1423-1436.
- 38.** Lohokare H, Bhole Y, Taralkar S, Kharul U. Poly(acrylonitrile) based ultrafiltration membranes: Optimization of preparation parameters. *Desalination*. 2011;282:46-53.

- 39.** Lai CL, Chao WC, Hung WS, et al. Physicochemical effects of hydrolyzed asymmetric polyacrylonitrile membrane microstructure on dehydrating butanol. *Journal of Membrane Science*. 2015;490:275-281.
- 40.** Ma X, Yang Z, Yao Z, Guo H, Xu Z, Tang CY. Tuning roughness features of thin film composite polyamide membranes for simultaneously enhanced permeability, selectivity and anti-fouling performance. *Journal of Colloid and Interface Science*. 2019;540:382-388.
- 41.** Chai GY, Krantz WB. Formation and characterization of polyamide membranes via interfacial polymerization. *Journal of Membrane Science*. 1994;93(2):175-192.
- 42.** Kolasinska M, Warszynski P. The effect of support material and conditioning on wettability of PAH/PSS multilayer films. *Bioelectrochemistry*. Apr 2005;66(1-2):65-70.
- 43.** Khare VP, Greenberg AR, Krantz WB. Development of pendant drop mechanical analysis as a technique for determining the stress-relaxation and water-permeation properties of interfacially polymerized barrier layers. *J. Appl. Polym. Sci.* Dec 2003;90(10):2618-2628.
- 44.** Freger V, Srebnik S. Mathematical model of charge and density distributions in interfacial polymerization of thin films. *J. Appl. Polym. Sci.* May 2003;88(5):1162-1169.
- 45.** Tang CY, She Q, Lay WCL, Wang R, Fane AG. Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration. *Journal of Membrane Science*. 2010;354(1-2):123-133.
- 46.** McCutcheon JR, Elimelech M. Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. *Journal of Membrane Science*. 2006;284(1):237-247.
- 47.** Li Z, Liu X, Chen G, Deng BL, Li WY. Effects of membrane morphology on the rejection of oil droplets: Theoretical analysis based on network modeling. *Journal of Membrane Science*. Oct 2019;588.
- 48.** Li W, Gao Y, Tang CY. Network modeling for studying the effect of support structure on internal concentration polarization during forward osmosis: Model development and theoretical analysis with FEM. *Journal of Membrane Science*. 2011;379(1-2):307-321.