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**Unique roles of aminosilane in developing anti-fouling thin film composite (TFC)
membranes for pressure retarded osmosis (PRO)**

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Abstract

Pressure retarded osmosis (PRO) has been identified as a promising technology to harvest the salinity gradient energy. For practical applications of PRO process, membrane fouling is a challenging issue as it leads to severe decline of PRO performance in terms of water flux and power density. It is imperative to develop anti-fouling membranes for PRO process. The current study demonstrated the unique roles and the great potential of aminosilane in developing anti-fouling thin film composite (TFC) PRO membranes. Experimental results revealed that aminosilane as a grafting agent can modify both the support layer (interior) and the selective layer of PRO membranes with remarkably enhanced hydrophilicity via a very simple grafting procedure. In the grafting, aminosilane was able to minimize the pore-blocking issue with almost no increase in the membrane structural parameter (S). Meanwhile, the membrane mechanical strength was well maintained with the grafting due to the capability of aminosilane as a cross-linker. With enhanced hydrophilicity, it was interestingly found that the water permeability (A) was doubled, while the salt rejection was maintained nearly unchanged. The combination of these effects brought in remarkably enhanced water flux, power density and anti-fouling property to the resultant membrane.

Keywords: pressure retarded osmosis (PRO); aminosilane; grafting; hydrophilicity; anti-fouling.

1. Introduction

Salinity gradients available from salt concentration difference between fresh water and salty water have been identified as one of the renewable and clean energy resources for sustainable development [1, 2]. Pressure retarded osmosis (PRO) proposed by Loeb [3] is one of the most promising technologies for harvesting the salinity-gradient energy and has attracted increasing attention for its great potential in addressing the water and energy related issues [1, 2, 4-6]. In PRO, water from a low salinity stream (feed water) permeates through a semi-permeable membrane to a pressurized high salinity stream (draw solution) that can further drive a turbine for power generation [7].

In practical applications, membrane fouling has been recognized to be one of the major factors limiting the PRO performance [8-13]. Compared to the fouling in conventional pressure-driven processes such as reverse osmosis (RO), membrane fouling in PRO is more complicated and its control is more challenging, given the fact that the PRO is typically operated with the membrane support layer facing the feed water [8-13]. In this membrane orientation, the foulants in the feed water can penetrate into the porous support layer, which would further cause severe internal fouling when the foulants clog the pores of the support layer and/or deposit on the back surface of the active layer [10, 11, 13]. To mitigate the internal fouling within the support layer of PRO membrane, one of feasible strategies is to modify the properties of PRO membrane support layer to reduce its affinity with the foulant [13]. However, there were limited relevant works reported in the literature [14].

In general, a membrane with greater hydrophilicity is less prone to fouling due to stronger repulsive foulant-membrane interaction [13, 15-19]. In this regard, improving the hydrophilicity of the PRO membrane (particularly the support layer) could be of great help to improve the membrane anti-fouling properties, for which grafting has been demonstrated to be a useful technique [14, 15, 20-23]. When using the grafting technique for PRO membrane modification/fabrication, several issues must be further addressed. Firstly, the hydrophilic treatment via grafting should be applied on the interior of membrane support in addition to the membrane surface, since the internal membrane fouling is a major concern in PRO process. Secondly, grafting within the membrane support layer may cause a potential problem of pore-blocking, resulting in an increase in the structural parameter of the membrane support. Thirdly, grafting usually involves a complicated multi-step procedure and is not easy to operate in practice. To overcome above issues, it is essential to select a suitable grafting agent, which (1) can offer a hydrophilic nature after grafting, (2) possesses a small size to minimize pore blocking, and (3) has simple and direct reaction with both membrane support and active layer.

Considering the above, aminosilane such as 3-aminopropyltrimethoxysilane (APTMS) is of interest to us. Aminosilane consists of both alkoxy and aminoalkyl groups connected to the Si atom, initially known as a precursor in the process of silanization and then extensively used in composites and adhesive formulations [24]. The hydrolysis of the alkoxy groups of aminosilane can lead to the generation of hydroxyl groups that offer a hydrophilic nature. Meanwhile, the active aminoalkyl groups of aminosilane give it potential to be grafted with membranes containing aromatic imide groups by a simple reaction such as aminolysis. For example, imide ring-opening reaction has been well reported as an efficient grafting method for fabricating

functional membranes based on aromatic imide polymers [25, 26]. Coincidentally, aromatic imide polymers such as Ultem[®] 1000 polyetherimide (PEI) [27, 28], Torlon[®] 4000T–MV poly(amide-imide) (PAI) [29] and Matrimid[®] 5218 polyimide (PI) [30] are widely used for the fabrication of PRO membranes. All of these suggest that aminosilane can be a suitable grafting agent in developing anti-fouling thin film composite (TFC) PRO membranes via grafting technique.

In the current study, APTMS-grafted PEI TFC PRO hollow fiber membrane was fabricated and evaluated to demonstrate the unique roles and great potential of aminosilane in the development of anti-fouling membranes for PRO application.

2. Experimental

2.1. Materials and chemicals

The commercially available aromatic imide polymer, Ultem[®] 1000 polyetherimide (PEI, General Electric Plastics) was selected as the polymeric material for membrane fabrication. The commercially available aminosilane, 3-aminopropyltrimethoxysilane (APTMS, >97%, CAS#13822-56-5, Sigma-Aldrich) was selected as the grafting precursor. *N*-Methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck) was used as a solvent for dope preparation. Lithium chloride (LiCl, >99%, CAS#7447-41-8, Sigma-Aldrich) was used as a pore-former. Trimesoyl chloride (TMC, >99%, CAS#4422-95-1, Sigma-Aldrich) and *m*-phenylenediamine (MPD, >99%, CAS#108-45-2, Sigma-Aldrich) were used as monomers for the interfacial polymerization. Cyclohexane (CAS#110-82-7, Sigma-Aldrich) was used as a solvent for TMC. Glycerol (CAS#56-81-5, Merck) and Isopropyl alcohol (IPA, CAS#67-63-0,

Merck) were used as wetting solvents. Dextran ($C_6H_{10}O_5$)_n samples with different molecular weights (molecular weight from 1500 to 400,000 Da, CAS# 9004-54-0, Sigma-Aldrich) were used to determine the molecular weight cut-off (MWCO). Sodium chloride (NaCl, CAS# 7647-14-5, Merck) was used to prepare the draw solutions. Humic acid (CAS#68131-04-4, Sigma-Aldrich) was selected as model organic foulant to evaluate the membrane anti-fouling properties in the PRO fouling tests. Calcium chloride (CaCl₂, CAS#10043-52-4, Sigma-Aldrich) was used to adjust the background electrolyte composition of humic acid solutions. The deionized (DI) water was supplied by a Milli-Q system.

2.2. Membrane fabrication

The PEI hollow fiber membrane substrate in the current study was fabricated by the dry-jet wet spinning technique. The dope solution was prepared by dissolving the pre-dried PEI polymer and the LiCl additive in the NMP solvent with stirring at 60 °C. The resultant homogenous solution was then transferred into a stainless tank, and degassed under vacuum at room temperature before spinning. In the spinning process, the dope was extruded through a spinneret at a controlled rate by a gear pump and went through an air gap into a coagulation bath. The resultant PEI hollow fibers were then collected and stored in a water bath for at least 3 days to remove residual NMP solvent. The spinning conditions are listed in Table 1.

Subsequently, the polyamide (PA) selective layer was synthesized on the inner surface of the as-spun hollow fiber PEI substrate by the interfacial polymerization of *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) as monomers [27, 31-33] to produce the TFC PEI hollow fiber membrane.

Finally, the as-prepared TFC PEI hollow fiber membrane was entirely immersed in a mixed solution (IPA/water, wt. 1:1) of APTMS (2 wt.%) at 60 °C for 120 min to generate the APTMS-grafted TFC PEI hollow fiber membrane. The resultant membrane was stored in a water bath for at least 3 days to remove unreacted APTMS.

2.3. Membrane characterization

The pure water permeability (PWP) of the membrane substrate was examined by a cross flow filtration set-up at a constant pressure of 1.0 bar. The molecular weight cut-off (MWCO) (defined as the molecular weight at 90 % rejection) was measured on a Polymer Laboratories-GPC 50 Plus system. The overall porosity (ϵ) was determined through the gravimetric method. The dynamic contact angle was tested with a tensiometer (DCAT11 Dataphysics). And the mechanical strength was measured by a Zwick 0.5 kN universal testing machine. The detailed methods to determine the pure water permeability (PWP), molecular weight cut-off (MWCO), overall porosity (ϵ), dynamic contact angle and mechanical strength of hollow fibers are available from our previous publication [32]. The contact angle of the selective layer was measured by the sessile drop method coupled with digital image analysis (Contact Angle System OCA, DataPhysics Instruments GmbH). A field emission scanning electronic microscope (FESEM, JEOL JSM-7600F) equipped with an energy dispersive X-ray (EDX) spectrometer was used for morphological observation. ATR-FTIR spectra were collected by an IR Presitige-21 (Shimadzu) spectrometer over a scanning range of 650–4000 cm^{-1} with a resolution of 4.0 cm^{-1} .

2.4. Determination of water permeability, salt permeability and structural parameter

Prior to all the tests, 5 pieces of the TFC hollow fiber membranes were sealed in a Teflon module with an effective length of 22 cm. Based on the active layer, the effective membrane area was estimated as 26 cm².

The water permeability A was determined in pressure-driven RO mode by pure water permeation tests with trans-membrane pressures varying from 0.5 to 1.5 bar. The feed water was pressurized through the lumen side of TFC hollow fiber membranes and the permeate water was collected from the shell side. The feed flow velocity was 0.71 m/s, and the corresponding Reynolds number (Re) was ~570. The salt rejection coefficient R_s was measured by permeation tests with 500 or 2000 ppm NaCl as the feed solution at 1.0 or 5.0 bar, respectively. The salt permeability B was then calculated by Eq. (1).

$$B = A(\Delta P - \Delta \pi) \frac{1 - R_s}{R_s} \quad (1)$$

where ΔP and $\Delta \pi$ are the hydraulic and osmotic pressure differences across the membrane, respectively.

The structural parameter S was determined by the mass transfer coefficient K_m ($S = D/K_m$, where D is the diffusivity of NaCl in water, 1.61×10^{-9} m²/s). The K_m was determined from FO tests with 0.25 M, 0.5 M, 0.75 M and 1.0 M NaCl as the draw solutions, respectively, and DI water as the feed, by using Eqs. (2) and (3) for the orientations of active layer facing draw solution (AL–DS) and feed water (AL–FW), respectively. All the measurements were carried out at ~23 °C.

$$J_w = K_m \ln \left(\frac{A\pi_D - J_w + B}{A\pi_F + B} \right) \quad (\mathbf{AL-DS}) \quad (2)$$

$$J_w = K_m \ln \left(\frac{A\pi_D + B}{A\pi_F + J_w + B} \right) \quad (\mathbf{AL-FW}) \quad (3)$$

2.5. PRO tests

PRO tests were performed in a lab-scale setup similar to the one reported elsewhere [8, 34]. The draw solution (1.0 M NaCl) was pressurized through the lumen side of TFC hollow fiber membranes, while the feed solution (DI water) flowed on the shell side. All the tests were carried out at ~23 °C. The water flux (J_w) was calculated by Eq. (4).

$$J_w = \frac{\Delta V_F}{A_m \Delta t} \quad (4)$$

where A_m is the effective area of the selective layer and V_F is the volume of the feed water. The power density (W) was calculated by the product of the water flux (J_w) and the corresponding trans-membrane pressure (ΔP), as expressed in Eq. (5).

$$W = J_w \times \Delta P \quad (5)$$

The reverse salt flux J_s was calculated using following equation:

$$J_s = \frac{\Delta(C_F V_F)}{A_m \Delta t} \quad (6)$$

where C_F is the salt concentration in feed water, which was determined by the corresponding conductivity.

2.6. Fouling tests

To study the membrane anti-fouling properties, short-term fouling experiments were

performed to evaluate the initial stage of fouling where foulant-membrane interaction plays a dominant role. After the fouling experiment, osmotic backwash was performed to investigate the membrane fouling reversibility. The whole experimental protocol consisted of the following steps. Firstly, the baseline test was performed at 9.0 bar using the foulant-free background electrolyte solution (containing 3 mM CaCl_2 and 10 mM NaCl) as feed solution and 1 M NaCl as draw solution. Then, 200 mg/L humic acid was introduced into the background feed solution to start the PRO membrane fouling test. A relatively high concentration of humic acid solution used in the current study was to accelerate the fouling rate. Thirdly, after the initial stage of fouling test, the fouled membranes were cleaned by osmotic backwash, where the active layer faced DI water while the draw solution (1.0 M NaCl) flowed on the shell side. Finally, the performance of the cleaned membrane was re-evaluated by repeating the first step. The fouling index (IF) which denotes the degree of membrane fouling was defined as Eq. 7 using a similar method reported elsewhere [23].

$$IF = \frac{J_{w,0} - J_w}{J_{w,0}} \quad (7)$$

where $J_{w,0}$ is the baseline water flux without humic acid and J_w is the final water flux after the fouling test. After osmotic backwash, the flux recovery ratio (FRR) which denotes the reversibility of membrane fouling was defined as Eq. 8.

$$FRR = \frac{J_{w,r} - J_w}{J_{w,0} - J_w} \times 100\% \quad (8)$$

where $J_{w,r}$ is the water flux after backwash; J_w is the water flux with humic acid; and $J_{w,0}$ is the original water flux without humic acid. The system temperature for all the tests was maintained at $\sim 23^\circ\text{C}$.

3. Results and discussion

3.1. Influence of APTM-grafting on PEI membrane substrate properties

Though the APTMS-grafting in the current study was proposed towards the entire TFC PEI hollow fiber membrane including the membrane substrate as well as the selective layer, the influence of APTMS on the membrane substrate needs a separate investigation first. The APTMS-grafting conditions for the substrate were the same as that for the entire TFC membrane as described in the Experimental section.

The characteristics of the PEI hollow fiber membrane substrate before and after the APTMS-grafting in terms of dimension, pure water permeability (PWP), molecular weight cut-off (MWCO), overall porosity (ϵ), dynamic contact angle and mechanical strength are comparatively listed in Table 2. For the original substrate, a high PWP of 386 L/m² h bar (LMH/bar) with a relatively low MWCO on the lumen side (161 kDa) was presented. Based on the log-normal distribution analysis [35] of the MWCO test, the mean pore size on the lumen surface was estimated as 10.01 nm with a geometric standard deviation of 1.31 while the pore size distribution was within 22 nm. And a high overall porosity (81%) was also exhibited. After APTMS-grafting, the PWP and MWCO were reduced to 331 LMH/bar and 90 kDa, respectively. The mean pore size on the lumen surface was reduced to 8.25 nm with a geometric standard deviation of 1.29 while the pore size distribution was within 18 nm. The porosity was almost the same (80%). All of these indicate that the structure of the membrane substrate did not change significantly after APTMS-grafting, which could also be confirmed by the morphological observation. As shown in Fig. 1, both the original and APTM-grafted PEI substrates show similar morphologies. After APTMS-grafting, the finger-like structure of the original substrate was well

maintained. The pore sizes on both outer and inner surfaces were only slightly reduced.

While grafting as a chemical modification technique may generally exert a negative impact on the mechanical strength, the current study found that the mechanical strength was not reduced but slightly enhanced after APTMS-grafting (refer to Table 2 for tensile modulus, stress at break and strain at break), despite the fact that the imide ring-opening reaction might decrease the rigidity of the PEI membrane substrate. This phenomenon could be attributed to the inter-chain crosslinking through Si–O–Si following APTMS-grafting, suggesting that APTMS as a grafting agent can simultaneously play a role as a cross-linker to maintain the mechanical strength of the PEI membrane substrate. This was confirmed by the ATR-FTIR analysis for the substrate before and after APTMS-grafting. As shown in Fig. 2, for the original substrate, the typical imide peaks of PEI at 1780 (symmetric C=O stretching vibration), 1720 (asymmetric C=O stretching vibration) and 1363 cm^{-1} (C–N–C stretching vibration) were presented. After APTMS-grafting, these imide peaks tended to diminish, indicating that the imide ring-opening reaction (as illustrated in Fig. 3) led to the transformation of the imide groups to amide groups. Moreover, the broad band around 3300 cm^{-1} (O–H stretching vibration) and the very strong peak at 1009 cm^{-1} (SiO–H deformation vibration) emerged with the grafting, suggesting the generation of silanol groups (Si–OH). In addition, the typical peak of asymmetric Si–O–Si stretching vibration at 1100 cm^{-1} [36] was observed, demonstrating that the inter-chain crosslinking had also taken place with the grafting. The enhanced mechanical strength of PEI membranes by APTMS grafting could also be confirmed in another experiment where PEI membrane was fabricated by blending APTMS with PEI in the dope casting solution. The results showed that using the APTMS blending method could improve the tensile modulus of the flat-sheet PEI membrane by over 70%.

Nevertheless, the APTMS blending method was not suitable for fabricating the PEI membranes in large scale, as the quick crosslinking between the PEI and the blended APTMS in the dope solution could result in the gel formation and significantly change the membrane structural and separation properties. In the current work, the APTMS grafting method can offer alternative solutions to the issues in blending method. The slightly enhanced mechanical strength (by 11.6% in terms of tensile modulus) of the APTMS-grafted PEI hollow fiber substrate may suggest a relatively mild crosslinking, which could be ascribed to that the less mobility of polymer chains in the already fabricated substrate may to some extent restrict the inter-chain crosslinking of silanol groups (Si–OH).

Moreover, the APTMS grafting can result in significantly enhanced membrane hydrophilicity. The surface dynamic contact angle (28°) of the grafted substrate was much lower than that (72°) of the original one (Table 2), which partly indicates the successful hydrophilic grafting while the internal hydrophilic situation of the substrate cannot be directly reflected by the surface dynamic contact angle. Considering its small size, APTMS should easily penetrate into the interior of the PEI membrane substrate to enhance the internal hydrophilicity, which was confirmed by SEM coupled with EDX analyses. It was found that the Si content was around 9.34, 7.46 and 6.28 wt.% at the outer surface, inner surface and the middle sponge-like section, respectively. On one hand, this result indicates that the interior of the membrane substrate is relatively less easy for grafting than the exterior. On the other hand, the Si content of as high as 6.28 wt.% at the middle section of the membrane substrate demonstrates a satisfying internal grafting, which is believed to be able to enhance the internal hydrophilicity due to the increased Si–OH groups.

3.2. Influence of APTM-grafting on polyamide selective layer properties

The role of APTMS in polyamide selective layer was investigated based on the entire APTMS-grafted TFC PEI hollow fiber membrane. The characteristics of the polyamide (PA) selective layer before and after grafting in terms of contact angle, water permeability (A), salt permeability (B) and structural parameter (S) are listed in Table 3, and the corresponding SEM morphologies are shown in Fig. 4. The original selective layer with a commonly observed morphology formed by the interfacial polymerization of MPD and TMC exhibited a typical polyamide contact angle of 50° . The A and B values were determined as 1.02 LMH/bar and 0.092 LMH, respectively, and the S value was 0.56 mm. After APTMS-grafting, the contact angle of the polyamide selective layer dropped to 25° , half of the original. Due to the enhanced hydrophilicity, it was interestingly found that the A value became more than 2 times as large as the original, while the salt rejection was still as high as 83.2%. The SEM coupled with EDX analysis confirmed the presence of Si on the selective layer with a content of 6.25 wt.%. This value is relatively lower than the aforementioned Si content of 7.46 wt.% on the inner surface of the APTMS-grafted PEI substrate, which could be attributed to the fact that amides are less reactive than imides in an aminolysis process. The S values of the membranes were determined using FO flux data (Fig. A1 in Appendix A). It was also found that there was nearly no increase in the S value for the APTMS-grafted membrane, suggesting that the potential problem of pore-blocking in the substrate was negligible in the APTMS-grafting process.

The polyamide selective layer before and after APTMS-grafting was further comparatively examined by the ATR-FTIR analysis. As shown in Fig. 5, both the original and grafted selective layers exhibited the characteristic peaks of amide at 1661 (C=O stretching vibration), 1531 (N-H

deformation vibration) and 1247 cm^{-1} (C–N stretching stretching). On the other hand, the broad band around 3300 cm^{-1} (O–H stretching vibration) and the strong peak at 1009 cm^{-1} (SiO–H deformation vibration) appeared after the grafting, similar to that observed in the ATR-FTIR of the APTMS-grafted PEI substrate. Meanwhile, the typical peak of asymmetric Si–O–Si stretching vibration at 1100 cm^{-1} was also similarly observed. A reasonable grafting mechanism for the polyamide selective layer may involve the amide exchange reaction as illustrated in Fig. 6. The above results suggests that APTMS could be used as the monomer instead of MPD for the interfacial polymerization with TMC to produce similar APTMS-grafted polyamide selective layer (Appendix B), which may provide different angles for fabricating the TFC membranes.

3.3. Impact of APTMS-grafting on PRO membrane performance

The PRO performance of the TFC PEI hollow fiber membrane before and after APTMS-grafting was evaluated, and the results are shown in Fig. 7. The water flux (J_w) of grafted membrane was enhanced by more than 100%, which is in consistence to the enhanced A value of more than 2 times as compared with the original one without APTMS-grafting (see Table 3). Observing the curves of water flux (J_w) versus applied trans-membrane pressure (ΔP), the J_w gradually declined with the increase of ΔP from 5 to 9 bar due to the reduced effective driving force. However, when ΔP further increased from 9 to 13 bar, the water flux tended to rise. Similar observation was also reported previously [27, 30]. This may be attributed to structural expansion of TFC hollow fiber membranes followed by an enlarged surface area, which further results in an increase in apparent A values [27, 30]. While the structural expansion in a sense helps for the enhancement of water flux, it indicates the onset of irreversible structure change, which weakens the membrane mechanical strength and leads to the final collapse of PRO membranes [37]. As a

result, PRO membranes should operate below the pressure of the “turning point” where the water flux stops declining, considering practical significance. A high “turning point” pressure is of course favorable for PRO membranes as it is closely related to the membrane mechanical strength. It was found that after APTMS-grafting, the turning point pressure did not decrease, suggesting that the mechanical strength of the PEI hollow fiber membrane can be well maintained after APTMS-grafting.

With the remarkable enhancement of the J_w , the power density (W) of the grafted membrane was enhanced accordingly by more than 100%. It was also found that the specific salt flux (J_s/J_w), which is the indicator of salt leakage from the draw solution, was also increased after APTMS-grafting when the applied trans-membrane pressure (ΔP) was above 9 bar. This observation could be due to the structural expansion as discussed previously. However, the specific salt flux can be well restrained below the turning point pressure. Moreover, even beyond the turning point pressure, the corresponding J_s/J_w values are still in a much lower range than those commercial membranes (i.e., > 0.1 M at the ΔP of ~ 12 bar) [34, 38], indicating the J_s/J_w -enhanced ICP effect was much less pronounced for the membranes fabricated in this study [13].

3.4. Impact of APTMS-grafting on PRO membrane anti-fouling behavior

Fig. 8 shows the flux behavior of the TFC PEI hollow fiber membrane before and after APTMS-grafting at the initial stage of fouling. The fouling experiments were performed under a severe fouling condition to accelerate the fouling rate where feed water contained 200 mg/L humic acid, 3 mM CaCl_2 and 10 mM NaCl. As shown in Fig. 8, a very steep water flux decline

due to internal fouling was observed for the original TFC PEI membrane with flux dropping by 28% within 60 min, exhibiting the fouling index (IF) of 0.28. In comparison, the corresponding water flux decline for the APTMS-grafted membrane was 16% and the IF was 0.16, only about half of the original. After the fouling experiments, osmotic backwash was immediately performed to investigate the fouling reversibility. A greater water flux recovery was observed for the APTMS-grafted membrane than the pristine membrane (i.e., 98% vs. 80%). According to Eq. 8, the flux recovery ratio (FRR) for the APTMS-grafted TFC PEI membrane was 88% while the FRR for the original TFC PEI membrane was only 29%. All of these observations demonstrate that the APTMS-grafted TFC PEI membrane has achieved an enhanced anti-fouling property, primarily due to the enhanced hydrophilicity in both of its support layer and active layer.

At the initial stage of membrane fouling, the foulant-membrane interaction plays a dominant role in the flux decline [13, 16]. When the membrane support layer is facing the feed water in the PRO process, foulant will enter into the porous support layer with the feed water convection and eventually rejected by the active layer. The internal fouling occurs with the attachment of foulant on the pore walls of the support layer and/or on the back surface of active layer [13]. As such, both the support layer properties and active layer properties play an important role in the foulant-membrane interaction. In the current study, the APTMS-grafted membrane shows significantly enhanced hydrophilicity in both its porous substrate and active layer, which provides the whole membrane from support to active layer with strong affinity to water and thus enhanced repulsion to humic acid molecules. As a result, humic acid would be less prone to attaching on the back surface of the active layer and/or within the support layer of the APTMS-grafted membrane, which accounts for its less flux decline in the fouling test and better

flux recovery in the backwashing.

4. Conclusions

The unique role of aminosilane as a capable grafting agent in developing anti-fouling TFC membranes for PRO process has been successfully demonstrated by the current work. The following findings are obtained from this study:

- (1) Aminosilane is able to simultaneously offer hydrophilicity to both the support layer (interior) and the selective layer of PRO membranes by a very simple grafting procedure.
- (2) Aminosilane is able to minimize the pore-blocking issue with almost no increase in the membrane structural parameter (S).
- (3) Aminosilane is able to act as a cross-linker to maintain the mechanical strength of PRO membranes during the grafting.
- (4) Aminosilane is able to remarkably enhance the water flux and the power density of the grafted PRO membranes.
- (5) Aminosilane is able to endue PRO membranes with a remarkably enhanced anti-fouling performance.
- (6) In addition, aminosilane is also able to play a role as a monomer for interfacial polymerization to directly construct an unprecedented organic-inorganic hybrid polyamide selective layer.

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Appendix A. FO performance of the original and modified membranes

Fig. A1 shows the FO performance of the original membrane, APTMS-grafted membrane, and the APTMS/TMC polyamide membrane. It was observed that the water flux of the grafted membrane was enhanced significantly (by ca. 48% on average), which are in accordance with the permeation results listed in Table 3. In addition, the membrane S value was determined using these FO results according to Section 2.4.

Fig. A1

Appendix B. Use of APTMS as monomer for interfacial polymerization

As discussed in Section 3.2, APTMS may be a candidate as monomer for interfacial polymerization to form TFC membrane. To confirm this speculation, the relevant interfacial polymerization was conducted using equivalent APTMS as the monomer to replace MPD. Interestingly, the expected similar APTMS-grafted polyamide selective layer was successfully obtained. Its characteristics in terms of contact angle, water permeability (A) and salt permeability (B) are listed in the last row of Table 3. Its ATR-FTIR spectrum is shown in Fig. 5 and its SEM morphology is presented in Fig. B1. It was found that the resultant contact angle, water permeability, salt permeability and ATR-FTIR spectrum are all similar to those of the APTMS-grafted polyamide selective layer. The SEM coupled with EDX analysis revealed that the content of Si in the selective layer was around 11.15 wt.%, which was expectedly higher than that (6.25 wt.%) of the APTMS-grafted polyamide selective layer due to the direct polymerization rather than grafting. It was also noticed that the APTMS/TMC polyamide selective layer as an organic-inorganic hybrid exhibited some distinct morphological features

from conventional polyamide selective layers, such as MPD/TMC, PPD/TMC, BDSA/TMC, MPD/BTEC, MPD/IPC, etc. [39]. For instance, it is interesting that nanoparticles with the size of around 20 nm can be observed on the APTMS/TMC polyamide selective layer (Fig. B1c). FO testing results are shown in Fig. A1c. The presented water flux of the APTMS/TMC polyamide selective layer was similar to the APTMS-grafted MPD/TMC polyamide selective layer (Fig. A1b), because of their similar A and B values as shown in Table 3. The structural parameter (S) was unchanged (0.56 mm (Table 3)) in comparison with the original membrane with MPD/TMC polyamide selective layer, due to the same membrane substrate used.

Fig. B1

Additionally, the PRO performance of the APTMS/TMC TFC PEI hollow fiber membrane was also evaluated in comparison to the original MPD/TMC TFC PEI hollow fiber membrane, as shown in Fig. B2. Improved water flux and power density were observed for the APTMS/TMC membrane compared to the original membrane, suggesting the potential advantage of the APTMS/TMC membrane.

Fig. B2

References

- [1] G.Z. Ramon, B.J. Feinberg, E.M.V. Hoek, Membrane-based production of salinity-gradient power, *Energy and Environmental Science*, 4 (2011) 4423-4434.
- [2] B.E. Logan, M. Elimelech, Membrane-based processes for sustainable power generation using water, *Nature*, 488 (2012) 313-319.
- [3] S. Loeb, Osmotic power plants, *Science*, 189 (1975) 654-655.
- [4] C. Klaysom, T.Y. Cath, T. Depuydt, I.F.J. Vankelecom, Forward and pressure retarded osmosis: potential solutions for global challenges in energy and water supply, *Chemical Society Reviews*, 42 (2013) 6959-6989.
- [5] F. Helfer, C. Lemckert, Y.G. Anissimov, Osmotic power with Pressure Retarded Osmosis: Theory, performance and trends – A review, *Journal of Membrane Science*, 453 (2014) 337-358.
- [6] A. Altaee, A. Sharif, Pressure retarded osmosis: Advancement in the process applications for power generation and desalination, *Desalination*, 356 (2015) 31-46.
- [7] S. Loeb, F. Van Hessen, D. Shahaf, Production of energy from concentrated brines by pressure retarded osmosis. II. Experimental results and projected energy costs, *Journal of Membrane Science*, 1 (1976) 249-269.
- [8] Q. She, Y.K.W. Wong, S. Zhao, C.Y. Tang, Organic fouling in pressure retarded osmosis: Experiments, mechanisms and implications, *Journal of Membrane Science*, 428 (2013) 181-189.
- [9] W.R. Thelin, E. Sivertsen, T. Holt, G. Brekke, Natural organic matter fouling in pressure retarded osmosis, *Journal of Membrane Science*, 438 (2013) 46-56.
- [10] N.Y. Yip, M. Elimelech, Influence of natural organic matter fouling and osmotic backwash on pressure retarded osmosis energy production from natural salinity gradients, *Environmental Science and Technology*, 47 (2013) 12607-12616.
- [11] M. Zhang, D. Hou, Q. She, C.Y. Tang, Gypsum scaling in pressure retarded osmosis: Experiments, mechanisms and implications, *Water Research*, 48 (2014) 387-395.
- [12] S.C. Chen, C.F. Wan, T.S. Chung, Enhanced fouling by inorganic and organic foulants on pressure retarded osmosis (PRO) hollow fiber membranes under high pressures, *Journal of Membrane Science*, 479 (2015) 190-203.
- [13] Q. She, R. Wang, A.G. Fane, C.Y. Tang, Membrane fouling in osmotically driven membrane processes: A review, *Journal of Membrane Science*, 499 (2016) 201-233.
- [14] X. Li, T. Cai, T.S. Chung, Anti-Fouling behavior of hyperbranched polyglycerol-grafted poly(ether sulfone) hollow fiber membranes for osmotic power generation, *Environmental Science and Technology*, 48 (2014) 9898-9907.
- [15] D. Rana, T. Matsura, Surface modifications for antifouling membranes, *Chemical Reviews*, 110 (2010) 2448-2471.
- [16] C.Y. Tang, T.H. Chong, A.G. Fane, Colloidal interactions and fouling of NF and RO membranes: A review, *Advances in Colloid and Interface Science*, 164 (2011) 126-143.
- [17] G. Zuo, R. Wang, Novel membrane surface modification to enhance anti-oil fouling property for membrane distillation application, *Journal of Membrane Science*, 447 (2013) 26-35.
- [18] A. Tiraferri, Y. Kang, E.P. Giannelis, M. Elimelech, Superhydrophilic thin-film composite forward osmosis membranes for organic fouling control: Fouling behavior and antifouling mechanisms, *Environmental Science and Technology*, 46 (2012) 11135-11144.
- [19] X. Lu, S. Romero-Vargas Castrillón, D.L. Shaffer, J. Ma, M. Elimelech, In Situ Surface Chemical Modification of Thin-Film Composite Forward Osmosis Membranes for Enhanced Organic Fouling Resistance, *Environmental Science & Technology*, 47 (2013) 12219-12228.

- [20] X. Wei, R. Wang, Z. Li, A.G. Fane, Development of a novel electrophoresis-UV grafting technique to modify PES UF membranes used for NOM removal, *Journal of Membrane Science*, 273 (2006) 47-57.
- [21] V.M. Kochkodan, V.K. Sharma, Graft polymerization and plasma treatment of polymer membranes for fouling reduction: A review, *Journal of Environmental Science and Health, Part A*, 47 (2012) 1713-1727.
- [22] M. Ulbricht, H. Matuschewski, A. Oechel, H.-G. Hicke, Photo-induced graft polymerization surface modifications for the preparation of hydrophilic and low-protein-adsorbing ultrafiltration membranes, *Journal of Membrane Science*, 115 (1996) 31-47.
- [23] S. Romero-Vargas Castrillón, X. Lu, D.L. Shaffer, M. Elimelech, Amine enrichment and poly(ethylene glycol) (PEG) surface modification of thin-film composite forward osmosis membranes for organic fouling control, *Journal of Membrane Science*, 450 (2014) 331-339.
- [24] Y. Xie, C.A.S. Hill, Z. Xiao, H. Miltz, C. Mai, Silane coupling agents used for natural fiber/polymer composites: A review, *Composites Part A: Applied Science and Manufacturing*, 41 (2010) 806-819.
- [25] L. Setiawan, R. Wang, K. Li, A.G. Fane, Fabrication of novel poly(amide-imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer, *Journal of Membrane Science*, 369 (2011) 196-205.
- [26] Y. Zhang, R. Wang, L. Zhang, A.G. Fane, Novel single-step hydrophobic modification of polymeric hollow fiber membranes containing imide groups: Its potential for membrane contactor application, *Separation and Purification Technology*, 101 (2012) 76-84.
- [27] S. Chou, R. Wang, A.G. Fane, Robust and High performance hollow fiber membranes for energy harvesting from salinity gradients by pressure retarded osmosis, *Journal of Membrane Science*, 448 (2013) 44-54.
- [28] Y. Li, R. Wang, S. Qi, C. Tang, Structural stability and mass transfer properties of pressure retarded osmosis (PRO) membrane under high operating pressures, *Journal of Membrane Science*, 488 (2015) 143-153.
- [29] X. Li, S. Zhang, F. Fu, T.S. Chung, Deformation and reinforcement of thin-film composite (TFC) polyamide-imide (PAI) membranes for osmotic power generation, *Journal of Membrane Science*, 434 (2013) 204-217.
- [30] G. Han, P. Wang, T.S. Chung, Highly robust thin-film composite pressure retarded osmosis (PRO) hollow fiber membranes with high power densities for renewable salinity-gradient energy generation, *Environmental Science and Technology*, 47 (2013) 8070-8077.
- [31] S. Chou, R. Wang, L. Shi, Q. She, C. Tang, A.G. Fane, Thin-film composite hollow fiber membranes for pressure retarded osmosis (PRO) process with high power density, *Journal of Membrane Science*, 389 (2012) 25-33.
- [32] R. Wang, L. Shi, C.Y. Tang, S. Chou, C. Qiu, A.G. Fane, Characterization of novel forward osmosis hollow fiber membranes, *Journal of Membrane Science*, 355 (2010) 158-167.
- [33] M. Tian, R. Wang, K. Goh, Y. Liao, A.G. Fane, Synthesis and characterization of high-performance novel thin film nanocomposite PRO membranes with tiered nanofiber support reinforced by functionalized carbon nanotubes, *Journal of Membrane Science*, 486 (2015) 151-160.
- [34] Q. She, D. Hou, J. Liu, K.H. Tan, C.Y. Tang, Effect of feed spacer induced membrane deformation on the performance of pressure retarded osmosis (PRO): Implications for PRO process operation, *Journal of Membrane Science*, 445 (2013) 170-182.
- [35] J. Ren, R. Wang, H.-Y. Zhang, Z. Li, D.T. Liang, J.H. Tay, Effect of PVDF dope rheology on

the structure of hollow fiber membranes used for CO₂ capture, *Journal of Membrane Science*, 281 (2006) 334-344.

[36] A. Alessi, S. Agnello, G. Buscarino, F.M. Gelardi, Raman and IR investigation of silica nanoparticles structure, *Journal of Non-Crystalline Solids*, 362 (2013) 20-24.

[37] Y. Chen, L. Setiawan, R. Wang, Identification of safe and stable operation conditions for pressure retarded osmosis with high performance hollow fiber membrane, *Journal of Membrane Science*, accepted (2015).

[38] Q. She, X. Jin, C.Y. Tang, Osmotic power production from salinity gradient resource by pressure retarded osmosis: Effects of operating conditions and reverse solute diffusion, *Journal of Membrane Science*, 401-402 (2012) 262-273.

[39] I.L. Alsvik, M.B. Hägg, Pressure retarded osmosis and forward osmosis membranes: Materials and methods, *Polymers* 5 (2013) 303-327.

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Fig. B1. Morphologies of the APTMS/TMC polyamide selective layer: (a) enlarged at 1,000×; (b) enlarged at 10,000×; (c) enlarged at 50,000×; (d) the cross section view.

Fig. B2. PRO performance comparison between the APTMS/TMC TFC PEI hollow fiber membrane (pink) and the original MPD/TMC TFC PEI hollow fiber membrane (blue).