Controllable Interfacial Polymerization for Nanofiltration Membrane Performance Improvement by the Polyphenol Interlayer

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Supporting Information

ABSTRACT: It is a huge challenge to have a controllable interfacial polymerization in the fabrication process of nanofiltration (NF) membranes. In this work, a polyphenol interlayer consisting of polyethyleneimine (PEI)/tannic acid (TA) was simply assembled on the polysulfone (PSf) substrate to fine-tune the interfacial polymerization process, without additional changes to the typical NF membrane fabrication procedures. In addition, three decisive factors in the interfacial polymerization process were examined, including the diffusion kinetics of fluorescence-labeled piperazine (FITC-PIP), the spreading behavior of the hexane solution containing acyl chloride, and the polyamide layer formation on the porous substrate by in situ Fourier transform infrared (FT-IR) spectroscopy. The experimental results demonstrate that the diffusion kinetics of FITC-PIP is greatly reduced, and the spreading behavior of the hexane solution is also impeded to some extent. Furthermore, in situ FT-IR spectroscopy demonstrates that by the mitigation of this PEI/TA interlayer, the interfacial polymerization process is greatly controlled. Moreover, the as-prepared NF membrane exhibits an increased water permeation flux of 65 L m⁻² h⁻¹ (at the operation pressure of 0.6 MPa), high Na₂SO₄ rejection of >99%, and excellent long-term structural stability.

1. INTRODUCTION

Nanofiltration (NF) membranes are widely applied in the fields of pollutants removal, compound refinement, and water treatment.¹⁻³ Although several traditional methods like evaporation and distillation can meet the basic needs for industrial usage, they are still energy-consuming and usually involve tedious procedures. In contrast, the NF process is highly energy-efficient and could be take place at low pressure, attracting a lot of attention both in academic and industrial fields.⁴⁻⁷ The typical NF membranes have a classical thin-film composite (TFC) structure and are prepared via interfacial polymerization process, where the diamine and acyl chloride monomers react at the water/oil interface.⁸⁻⁹ In general, the NF performance could be optimized by two effective methods, including regulating the formed polyamide selective layer and/or the porous substrate separately to get the maximum NF performance.¹⁰⁻¹³ Nevertheless, interfacial polymerization taking place directly on the traditional substrates always suffers from rapid and uncontrollable reaction, resulting in an uneven and defective polyamide selective layer and a possible deterioration of the NF performance. To optimize substrate properties, researchers have made numerous efforts to adjust the porous structure and/or the substrate surface wettability. Several methods have been proposed in the past decades by the researchers, which include increasing the substrate porosity,¹⁴ blending the hydrophilic additives in the substrates,¹⁵ and/or modifying the substrate surface wettability.¹⁶ However, a detailed interfacial polymerization process investigation still remains like a “black box” because of difficulty in acquiring quantitative measurements of this rapid reaction rate (usually completed within several seconds). Recently, to potentially decrease the interfacial polymerization reaction rate and reduce the formed polyamide layer thickness, Livingston and his co-workers have fabricated a defect-free, sub-10 nm
polyamide selective layer by introducing Cd(OH)$_2$ nanowires as a sacrificial layer.$^{17}$ At the same time, our group creatively used carbon nanotubes and/or cellulose nanocrystals as an interlayer, which is placed between the porous substrate and the polyamide selective layer.$^{18,19}$ It is confirmed theoretically that these interlayers could adsorb more diamine monomer by the enhanced Laplace pressure and cause reinforced interactions between the diamine monomer and porous substrates. Although the interlayers lead to reduced diamine monomer releasing from the aqueous to hexane phase,$^{20,21}$ it is still a great challenge to deeply understand the effects of these interlayers on the interfacial polymerization process.

Tannic acid (TA), as a naturally derived product, has been widely used for surface modification because of its abundant hydroxyl groups, sufficient hydrogen-bonding interactions, and easy postreaction process.$^{22−27}$ In the reported literatures, polyethyleneimine (PEI) is usually applied to ensure a good adhesion between the substrate and TA molecules through the abundant electrostatic and hydrogen-bonding interactions. Here, in this work, in the fabrication process of NF membrane, PEI/TA layer is simply constructed as an interlayer between the porous substrate and the polyamide selective layer, as schematically shown in Figure 1. In addition, three decisive factors in the interfacial polymerization process are examined, including the diffusion kinetics of the fluorescein-labeled piperazine (FITC-PIP), the spreading behavior of the hexane solution containing acyl chloride, and the polyamide layer formation process taking place on the porous substrate. The experimental results demonstrate that the FITC-PIP diffusion kinetics is greatly reduced and the spreading of the hexane solution is also impeded to some extent. In addition, in situ Fourier transform infrared (FT-IR) spectroscopy demonstrates that by the mitigation of this PEI/TA interlayer, the interfacial polymerization process is well controlled. Moreover, the as-prepared NF membrane exhibits a doubled water permeation flux of 65 L m$^{-2}$ h$^{-1}$ (the operation pressure is 0.6 MPa), compared with the typical NF membrane without the PEI/TA interlayer, high Na$_2$SO$_4$ rejection of >99%, and excellent structural stability after swelling in ethanol for several hours.

2. RESULTS AND DISCUSSION

2.1. Fabrication of PEI/TA-Modified Substrate. The procedure to assemble PEI/TA was carried out in acidic, neutral, and basic solutions and are shown in the digital photos in Figure S1 in the Supporting Information. The results indicate that PEI/TA assembled well in the neutral solution (about pH $\sim 7.5$) through multiple electrostatic and hydrogen-bonding interactions. At first, a nascent PSf substrate with a negative charge of the $\zeta$-potential of about $-38$ mV was immersed in a positively charged PEI solution (concentration is fixed at 2 mg/mL and $\zeta$-potential is $36$ mV) to ensure an electrostatic adhesion between the PSf substrate surface and TA molecules (Figure S2 in the Supporting Information). Then, effects of TA concentration and total assembly time on the PEI/TA deposition degree (DD) (%) on the nascent PSf substrate are investigated. It is shown that the PEI/TA deposition degree (%) increases from 2 to 7 wt %, while the TA concentration increases from 1 to 4 mg/mL and then declines to 6 wt %, when the TA concentration is 5 mg/mL (when the total immersion time is 6 min) (as shown in Figure S3a in the Supporting Information). In a similar way, the PEI/TA deposition degree (%) increases from 3 to 8 wt % as the total assembling time for PEI/TA increases from 2 to 6 min and remains stable from 6 to 10 min (Figure S3b in the Supporting Information, when the PEI concentration is fixed at 2 mg/mL and the TA concentration at 4 mg/mL). As a result, the nascent PSf substrate was modified by the PEI/TA assembling process with optimized experimental conditions of PEI = 2 mg/mL, TA = 4 mg/mL, and total assembly time = 6 min.

The surface and cross-sectional morphologies of PEI/TA-modified substrates were observed by field emission scanning electron microscopy (FESEM) (Figures S4 and S5 in the Supporting Information). It is shown that the PEI/TA-modified substrate surfaces are uniform and smooth, with decreased surface pores and occasional small aggregates. In addition, the surface hydrophilicity is obviously enhanced in the PEI/TA-modified layer, which is demonstrated by a decrease in the water contact angle (WCA) from 70 ± 8° of the nascent PSf substrate to 25 ± 3° of the PEI/TA-modified substrate (shown in Figure S6 in the Supporting Information). The above-mentioned substrate properties, including the improved surface morphologies and increased hydrophilicity, are expected to endow PEI/TA-modified substrates with the ability to efficiently absorb a PIP monomer in aqueous solution.

2.2. Effect of PEI/TA-Modified Layer on the FITC-PIP Diffusion Kinetics. During the interfacial polymerization process, diamine monomer diffusion is the rate-determining step because the interfacial reaction rate is much larger than the diamine monomer diffusion rate. Nevertheless, methods to detect PIP are usually limited due to difficulty in labeling PIP due to the lack of appropriate UV–vis absorbance. Here,
fluorescence labeled method was used to conveniently monitor the FITC-PIP diffusion kinetics from aqueous to hexane phase through substrates. The fluorescence labeling procedure and UV-vis detection results are schematically shown in Figure 2. The results indicate that for nascent PSf substrate, the FITC-PIP monomer diffuses through the substrate fast in the initial diffusion stage, then gradually reduces, and reaches a plateau. Nevertheless, for the PEI/TA-modified substrate, the FITC-PIP diffusion concentration through the substrate is greatly depressed by interactions between FITC-PIP and PEI/TA-modified substrate and the blockage of substrate pores by the PEI/TA-modified layer. The concentration in the hexane phase at the diffusion time of 60 s is reduced from 0.035 to 0.005 (mg/mL), and the correspondingly calculated diffusion rate, $k_1$, of PEI/TA-modified substrate decreases from $6.133 \times 10^{-4}$ to $6.617 \times 10^{-5}$ (mg/mL s) compared with that of the nascent PSf substrate.

According to the theoretical kinetic model of the interfacial polymerization process, if the diamine diffusion rate reduces, the thickness of the formed polyamide layer will also decrease. The polyamide layer thickness can be estimated both from the cross-sectional FESEM images (Figure S7 in the Supporting Information) and the inserted transmission electron microscopy (TEM) images in Figure 3, exhibiting that the polyamide layer thickness reduces from about $134 \pm 6$ nm for PSf NF to $82 \pm 5$ nm for PEI/TA-PSf NF. Additionally, the reduced diamine diffusion rate also has obvious effect on membrane surface morphologies. For example, the FESEM images and the inserted TEM images in Figure 3 show that the polyamide surface of PSf NF is typically "nodular" ($R_{q} \sim 38.4$ nm from atomic force microscopy (AFM) analysis in Figure S8 and Table S1 in the Supporting Information) in the PIP/trimesoyl chloride (TMC) interfacial polymerization system. Moreover, the membrane surface of PEI/TA-PSf NF ($R_{q} \sim 22.7$ nm from the AFM analysis in Figure S8 and Table S1 in the Supporting Information) is smooth with fewer spherical convex than the surface of PSf NF, which could be ascribed to the retarded diamine diffusion and the mitigated interfacial reaction.

### 2.3. Effect of PEI/TA Layer on the Spreading Behavior of the Hexane Solution

According to Young’s equation, the spreading behavior of the hexane solution is related to interfacial tension as well as interfacial polymerization reaction process. As reported in the literature, to better understand the mechanism of interfacial polymerization, several studies have put forth the idea that a co-solvent is likely to promote diamine diffusion because it can reduce the solubility difference or interfacial tension between two immiscible solutions. However, detailed mechanism studies are still lacking. A typical interfacial polymerization to construct a polyamide layer involves two steps: the immersion and drying process of aqueous solution and then the hexane solution containing acyl chloride is gently poured on the substrate surface to form a polyamide layer in situ. Therefore, investigation of the spreading behavior of the hexane solution without or with reactive acyl chloride monomer is of great significance. We use the change in the oil contact angle (OCA) of the hexane solution with time to examine the effects of the PEI/TA layer on the spreading of the hexane solution and

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (a) Synthetic route of FITC-PIP. (b) FITC-PIP diffusion concentration from aqueous to organic phase (without acyl chloride in the organic phase) through the nascent PSf substrate or PEI/TA-modified substrate, respectively, as a function of diffusion time. (c) Resulting FITC-PIP diffusion rate $k_1$ with diffusion time.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** FESEM images of surface nodular morphologies of (a) PSf NF and (b) PEI/TA-PSf NF, with the inserted TEM images showing the polyamide layer structure and thickness. (c) Schematic illustration of the confined and suppressed diamine diffusion by modified PEI/TA interlayer.
the interfacial polymerization process, which are illustrated in Figures 4 and S9 in the Supporting Information, respectively. The results of the OCA measurements in Figure 4 and Table 1 show that as nascent PSf substrate is immersed in aqueous solution (without reactive diamine monomer), the OCA rapidly decreases from 27 to 0° only in 280 ms. Nevertheless, in the simulation of the interfacial polymerization process (diamine in the aqueous phase and acyl chloride in the hexane phase), the changing rate \( k_2 \) of the OCA decreases from 96.4 to 42.0 (°/s). This result could indicate that the OCA change is hindered by polyamide formation at the aqueous/hexane interface, which is in accordance with the measured interfacial tension in Figure S10 in the Supporting Information. Additionally, the PEI/TA layer would further reduce the changing rate \( k_2 \) of the OCA from 96.4 to 9.8 (°/s) (without reactive monomers in the solutions) and from 42.0 to 3.6 (°/s) (with diamine in the aqueous phase and acyl chloride in the hexane phase). The above experimental results give the information that during the interfacial polymerization process, the spreading behavior of the hexane solution is greatly hindered by the PEI/TA layer, which is consistent with the calculated increased substrate surface free energy in Table S2 in the Supporting Information.

Table 1. Quantitative Analysis of the OCA Changing Rate \( k_2 \) with the Hexane Solution Spreading on the Nascent PSf Substrate and the PEI/TA-Modified Substrate and with Reactive Monomers (Diamine in the Aqueous Phase and Acyl Chloride in the Organic Phase), Respectively

| Sample                          | \( \Delta \theta_o \) (°) | Time (ms) | \( k_2 \) (°/s) |
|---------------------------------|-------------------------|-----------|-----------------|
| Nascent PSf substrate (no reactive monomers) | 27                      | 280       | 96.4            |
| PEI/TA-modified substrate (no reactive monomers) | 22                      | 2250      | 9.8             |
| Nascent PSf substrate (diamine and acyl chloride) | 21                      | 500       | 42.0            |
| PEI/TA-modified substrate (diamine and acyl chloride) | 18                      | 5000      | 3.6             |

To quantitatively study the spreading behavior of solution, the co-coefficient \( S \) is introduced. If \( S > 0 \), it means the hexane oil drop spreads instantaneously on the substrate surface. On the contrary, when \( S < 0 \), the substrate surface is only partially wetted and exhibits an oil contact angle \( \theta \). According to Young’s equation: \( \gamma_{lg} \cos \theta + \gamma_{sa} = \gamma_{sg} \), where \( \gamma_{lg} \) of the organic solution hexane is fixed at 24 mN/m and the oil solution spreads fast on the nascent PSf substrate, thus \( \theta \) can be regard as \( \approx 0^\circ \). Therefore, the calculation of \( \gamma_{sa} = \gamma_{sg} - \gamma_{lg} \cos \theta \) is maintained at a constant of 30° and \( \gamma_{sa} = \gamma_{sg} - \gamma_{lg} \cos \theta' \) = -20.8 mN/m. Therefore, the difference \( \Delta S \) is calculated by \( S' \) of the PEI/TA-modified substrate minus \( S \) of the nascent PSf substrate, which can be regarded as \( \approx 0^\circ \). The quantifiable result shows that \( S' \) of the PEI/TA-modified substrate is less than that of the nascent PSf substrate, which commendably confirms that the spreading of hexane solution is impeded by the PEI/TA-modified layer to some extent.

### 2.4. Polyamide Formation Monitored by In Situ FT-IR Spectroscopy

As mentioned above, the PEI/TA-modified layer both reduces the FITC-PIP diffusion rate and retards the spreading of the hexane solution on the substrates. Nevertheless, the specific and quantifiable effect of the PEI/TA-modified layer...
on the polyamide formation process still lacks sufficient experimental proof because of the fast reaction and difficulty in directly studying the reaction taking place on the porous substrates. Here, in situ FT-IR spectroscopy is used to directly investigate the interfacial polymerization of the PIP/TMC...
system on the nascent PSf substrate and the PEI/TA-modified substrate (as shown in Figure 5).

The polyamide formation process is confirmed by the characteristic absorbance peaks in the FT-IR spectra, such as the C−N stretching at 1380 cm$^{-1}$, C=O stretching at 1420 cm$^{-1}$, and O−C−N stretching at 1640 cm$^{-1}$ (Figure S11 in the Supporting Information). The integral area of the absorbance peak at 1640 cm$^{-1}$ characterizes the O−C−N stretching and grows fast from 0 to 175 during the reaction time from 0 to 60 s, with the interfacial polymerization taking place on the nascent PSf substrate. After that, the peak area growth trend is slowed down between 60 and 200 s and tends to flatten after the reaction time of 200 s. However, in the case of the PEI/TA-modified substrate, the absorbance peak area increases gradually from 0 to 40 in the reaction time of 250 s, exhibiting an obviously suppressed growth trend. Furthermore, the calculated first-order derivative of the peak area with the reaction time exhibits the slope of the fitting line showing that $k_{PSF} = 1.83 \times 10^{-3}$ (s$^{-2}$) is higher than $k_{PEI/TA} = 3.84 \times 10^{-4}$ (s$^{-2}$). The experimental results rationally point out that the PEI/TA layer can potentially serve as a storage place for diamine monomer, resulting in the reduction of the diamine diffusion rate and partially mitigation of the interfacial polymerization process. The in situ FT-IR analyses (Figure S12 and Tables S3,S4 in the Supporting Information) transform the FT-IR absorbance into polyamide layer thickness, and the polyamide layer thickness values have good consistency with the cross-sectional images of FESEM and TEM (as shown in Figure 3) and further evince the tendency of polyamide layer thickness to decreasing after the introduction of the PEI/TA interlayer.

2.5. Structures, Properties, and Performance of NF Membranes. The chemical structures of NF membranes were analyzed by FT-IR/ATR and X-ray photoelectron spectrometer (XPS) spectra (shown in Figure S13 in the Supporting Information). Vibration peaks in the FT-IR/ATR spectra at 1064, 1350, 1469, 1480, and 1700 cm$^{-1}$ represent the formation of a polyamide layer on the nascent PSf substrate and PEI/TA-modified substrate surface. In Table S5 in the Supporting Information, it is shown that the N element increases when the O/N ratio decreases, with the formation of polyamide on the substrates. Compared with the formation of polyamide on the nascent PSf substrate, the cross-linking degree of polyamide produced on the PEI/TA-modified substrate increases from 50 to 73%, which suggests improved selectivity to inorganic salts.

Moreover, the WCA in Figure 6a decreases from 75° for PSF NF to 48° for PEI/TA-PSF NF. Besides, the $\zeta$-potential in Figure 6b increases from −38 mV for PSF NF to −8 mV for PEI/TA-PSF NF. As a result, this work has a profound impact on the betterment of NF membrane preparation and application.

3. CONCLUSIONS

In summary, in an interfacial polymerization fabrication process of NF membrane, the polyphenol PEI/TA interlayer has influences including (1) reducing the diamine diffusion rate; (2) impeding the organic solution spreading; and (3) mitigating the polyamide layer formation process. The optimized NF membrane performance includes both increased water permeation flux and enhanced salt rejection rate. As a result, this work has a profound impact on the betterment of NF membrane preparation and application.

4. EXPERIMENTAL SECTION

4.1. Materials. Polysulfone (PSf) ultrafiltration substrates were purchased from Shanghai Mega-Vision Membrane Engineering & Technology Co., Ltd. (China) with the molecular weight cutoff of 50 kDa. Branched polyethyleneimine (PEI, $M_w \sim 10,000$ Da), tannic acid (TA), and fluorescein isothiocyanate (FITC) were purchased from Aladdin Co., Ltd. (China). Piperazine (PIP), trimesoyl chloride (TMC), and N,N-bis-(2-hydroxyethyl) glycine (Bicine) were obtained from Sigma-Aldrich Co., Ltd. Moreover, ethanol, hexane, and other kind of inorganic salts were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). These chemicals were used without further purification. Deionized (DI) water used in the experiment was produced from a lab instrument of ELGA Lab water purification system (France).
4.2. Preparation of NF Membranes. Nascent PSf substrates were first immersed in ethanol for 12 h and then washed in DI water for 1 h in order to thoroughly remove impurities in substrate pores. Branched polyethyleneimine (PEI) and tannic acid (TA) were dissolved in Bicin buffer solution (pH = 7.5), with the concentration of PEI fixed at 2 mg/mL and TA ranging from 1 to 5 mg/mL. PSf substrates were prewetted in ethanol for 30 min and fully immersed in PEI solution for 1, 2, 3, 4, and 5 min in order to absorb PEI coating on the substrate surface. After that, the substrates were taken out and washed thoroughly by DI water for three times. Consequently, the substrates were then immersed in TA solution for 1, 2, 3, 4, and 5 min to form a PEI/TA layer on the substrate surface. It is worth noticing that the immersion times of PEI and TA solutions were the same and the total assembly time was referred to as the sum of their immersion times. The PEI/TA-modified substrate was completely washed with DI water for three times to remove unbound PEI/TA monomers.

Traditional interfacial polymerization was carried out on the nascent PSf substrate and the PEI/TA-modified substrate using PIP and TMC as reactive monomers. At first, these substrates were upper-side immersed in 10 mL of 0.3 wt % PIP aqueous solution for 10 min. Then, after drying off in air for 30 min, the excessive PIP solution was removed from the substrate surface. After that, 10 mL of 0.3 wt % TMC dissolved in the hexane solution was then gently poured on the substrate to in situ form a polyamide layer on the substrate surface with a 2 min interfacial reaction time. Finally, the as-prepared NF membranes were rinsed with DI water for three times and then conserved in DI water for further membrane characterization.

To quantitatively measure the PEI/TA mass that assembled onto the PSf substrate surface, the PEI/TA deposition degree (DD, wt %) was defined according to eq 1

$$DD = \frac{W_1 - W_0}{W_0} \times 100\%$$

where $W_1$ is the total mass of the PEI/TA-modified substrate and $W_0$ is the mass of the nascent PSf substrate.

4.3. Fluorescence-Labeled Piperazine (FITC-PIP) Diffusion Kinetics. FITC-PIP is synthesized according to the literature and FITC reacted with PIP by the following procedures. A sample of 10 mg of PIP and 20 mg of FITC was added to 20 mL of ethanol in a round-bottom flask at room temperature. After stirring for 3 h, ethanol was removed by vacuum distillation and the resulting product was yellow green. After that, 10 mg of FITC-PIP was added into 20 mL of DI water to prepare the aqueous solution at a concentration of 0.5 mg/mL. UV—vis spectra were recorded using an ultraviolet spectrometer (UV 2450, Shimadzu, Japan) to monitor the FITC-PIP diffusion from the aqueous phase to the hexane phase through the nascent PSf substrate and PEI/TA-modified substrate. The experiment was performed with a home-made U-shaped device (the contact membrane area is 4 cm²). At first, 20 mL of aqueous solution of FITC-PIP was added in one side of the device. Then, the sample of 20 mL of hexane was added in another side of the device and a series of 3 mL of the hexane solution very close to the substrate surface was immediately taken out for UV—vis spectrometric determination. The detection interval is 10 s, until the diffusion time reaches 60 s. According to the fitting straight line of absorbance at 495 nm of FITC-PIP vs. diffused concentration in the hexane phase (shown in Figures S16 and S17 in the Supporting Information), the FITC-PIP diffusion rate from the aqueous phase to the hexane phase through the nascent PSf substrate and PEI/TA-modified substrate were calculated by eq 2

$$k_1 = \frac{\Delta c}{\Delta t}$$

where $k_1$ is the FITC-PIP diffusion rate from the aqueous phase to the hexane phase through the substrates, $\Delta c$ is the FITC-PIP concentration change in the hexane phase and $\Delta t$ is the corresponding diffusion time.

4.4. Quantitative Measurement of the Spreading Behavior of the Hexane Solution. To quantitatively study the spreading behavior of the hexane solution, dynamic oil contact angle (OCA) measurement was used. The experimental procedures were as follows: first, nascent PSf substrate and PEI/TA-modified substrate were fully impregnated with 10 mL of DI water for 10 min. After that, the substrate surfaces were wiped off with a filter paper and the remaining aqueous solution was reserved in the internal pores of the substrate, with no surface residual solution. Then, a sample of 10 µL of hexane droplet was gently dripped on the substrate surface to in situ monitor the OCA change as a function of time by using the contact angle measurement instrument (Surface-Meter, OSA 200, China), which was equipped with a high speed camera. To simulate the actual interfacial polymerization of the PIP/TMC interfacial reaction system, 0.3 wt % PIP and TMC reactive monomers were added into the aqueous and hexane phases, respectively. The OCA changing rate with spreading time is calculated by eq 3

$$k_2 = \frac{\Delta \theta_{oil}}{\Delta t}$$

where $k_2$ is the OCA change rate with the spreading time, $\Delta \theta_{oil}$ is the OCA change in the spreading process, and $\Delta t$ is the spreading time.

In addition, the spreading behavior of the hexane solution was quantitatively measured by the spreading coefficient $S$, which is defined by eq 4

$$S = \gamma_{sg} - \left( \gamma_{lg} + \gamma_{gl} \right)$$

where $S$ is the spreading coefficient, $\gamma$ is the interfacial tensions of the solid–gas ($\gamma_{sg}$), liquid–gas ($\gamma_{lg}$), and solid–liquid ($\gamma_{gl}$), respectively.

4.5. In Situ Monitoring of Polyamide Formation Process by FT-IR Spectroscopy. The polyamide formation was in situ monitored by using FT-IR spectroscopy (React IR 15, Mettler Toledo, Switzerland) on nascent PSf substrate and PEI/TA-modified substrate, respectively. The experimental procedures were as follows: the substrates were first installed in a home-made reactor and upper-side contacted with 0.3 wt % PIP solution (10 mL). After fully immersing in PIP solution for 10 min, the excessive aqueous solution on the substrate surface was carefully wiped off and removed by filter paper. The FT-IR absorbance data collection was instantaneously started by adding 0.3 wt % TMC solution (10 mL). The online FT-IR absorbance data with the reaction time were simultaneously collected through spectroscopic probe, which was placed tightly on the substrate surface (with the minimum sampling time interval of 15 s). Polyamide layer thickness was transformed from the characteristic FT-IR absorbance by the following eqs 5 and 6 reported in ref 51.
\[ d_p = \frac{\lambda}{2 \pi \sqrt{n_1^2 \sin^2 \theta - n_2^2}} \]  

(5)

where \( d_p \) is the infrared light penetration depth; \( \lambda \) is the wavelength of infrared radiations; and \( n_1 \) and \( n_2 \) are the refractive indices of the crystal and the sample, respectively. According to empirical parameters in the reference, \( n_1 = 4.0 \) (Ge crystal), \( n_2 = 1.50 \) (polyamide), and \( \theta = 45^\circ \), thus \( d_p = 0.066 \lambda \).

\[ T = -\ln \left[ \frac{A_b(T)}{A_b(0)} \right] \times \frac{d_p}{2} \]  

(6)

where \( T \) is the converted polyamide layer thickness and \( A_b(T) \) and \( A_b(0) \) are the absorbances of a characteristic band at the polyamide layer thicknesses of \( T \) and 0.

### 4.6. Performance Measurements of the NF Membranes

The NF performances including water permeation flux and inorganic salts rejection were measured and evaluated by a self-made cross-flow module equipment (with the effective contact membrane area \( \sim 7.04 \text{ cm}^2 \)) and electrical conductivity meter (Mettler Toledo, FE30K, Switzerland), respectively. Water permeation flux \( (F_{\text{w}} \text{ L/m}^2 \text{ h}) \) and salt rejection rate \( (R, \%) \) were calculated by eqs 7 and 8.

\[ F_w = \frac{Q}{t \times A} \]  

(7)

where \( Q, t, \) and \( A \) are the solution permeated volume, permeation time, and effective filtrated membrane area, respectively. Test experiment conditions include operation pressure of 0.6 MPa, temperature of 30 °C, and cross-flow rate of 30 L/h.

\[ R = \frac{1 - C_p}{C_f} \times 100\% \]  

(8)

where \( C_p \) and \( C_f \) are concentrations of inorganic salts in the permeate and feed solution sides, with the feed solution concentration fixed at 1000 mg/L.

Additionally, the long-term structural stability of the fabricated NF membranes was examined after being immersed and swelled in ethanol from 0 to 120 h. All the water permeation flux and the salt rejection rate were measured for three times and the average value of all the measured results is calculated.

### 4.7. Other Characterizations of the NF Membranes

The chemical structures, functional groups, and element compositions of membrane surface were characterized by FT-IR/ATR spectrometer (FT-IR/ATR, Nicolet 6700) and X-ray photoelectron spectrometer (XPS, PerkinElmer 5300). To investigate the extent of polyamide selective layer cross-linking, the XPS spectra were analyzed to calculate the cross-linking degree (%) by eqs 9 and 10.

\[ \frac{O}{N} = \frac{3m + 4n}{3m + 2n} \]  

(9)

\[ D (\%) = \frac{m}{m + n} \]  

(10)

where \( m \) and \( n \) are the cross-linked and linear parts of polyamide layer, respectively. \( D (\%) \) is the corresponding calculated cross-linking degree of the polyamide selective layer.

The surface and cross-sectional morphologies of the NF membranes were observed by field emission scanning electron microscopy (FESEM, Hitachi S4800, Japan). Polyamide layer structures were examined by transmission electron microscopy (TEM, Hitachi `7650, Japan), with the membrane samples embedded in the LR White Resin (London Resin Company, Reading, U.K.), cut by the ultramicrotome (Leica Microsystems, Wetzlar, Germany), and then mounted on copper grids for further observation. The surface topographies were observed by atomic force microscopy (AFM, Bruker Multi-Mode 8) in the tapping mode. Contact angles measuring the surface hydrophilicity were evaluated by a contact angle measuring instrument (Surface-Meter, OSA 200, China). Membrane surface charges were measured by the electrokinetic analyzer (SurPASS Zeta, Litesizer 500, Austria) with KCl (1 mmol/L). The stress–strain curves were examined by the tensile stress test instrument (RGM-4000, Shenzhen REGER Instrument Co., Ltd, China).

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01446.

**UV–vis analysis; \( \zeta \)-potential; PEI/TA deposition degree (wt %); surface and cross-sectional FESEM images; contact angle; AFM images; interfacial tensions; in situ FT-IR absorbance; FT-IR/ATR and XPS spectra; acid–alkali stability; stress–strain curves; and UV–vis absorbance (PDF)**

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**Notes**

The author declares no competing financial interest.

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### References

1. Miller, D. J.; Dreyer, D. R.; Bielawski, C. W.; Paul, D. R.; Freeman, B. D. Surface Modification of Water Purification Membranes. Angew. Chem., Int. Ed. 2017, 56, 4662–4711.

2. Liang, W.; Li, L.; Hou, J.; Shepherd, N. D.; Bennett, T. D.; D’Alessandro, D. M.; Chen, Y. Linking Defects, Hierarchical Porosity Generation and Desalination Performance in Metal–organic Frameworks. Chem. Sci. 2018, 9, 3508–3516.

3. Laberty-Robert, C.; Vallet, K.; Pereira, F.; Sanchez, C. Design and Properties of Functional Hybrid Organic-Inorganic Membranes for Fuel Cells. Chem. Soc. Rev. 2011, 40, 961–1005.

4. Lomadze, N.; Perez, M.; Prucker, O.; Ruhe, J.; Reinecke, H. Step-and-Repeat Assembly of Molecularly Controlled Ultrathin Polymamide Layers. Macromolecules 2010, 43, 9056–9062.

5. An, Q.-F.; Ji, Y.-L.; Hung, W.-S.; Lee, K.-R.; Gao, C. J. AMOC Positron Annihilation Study of Zwitterionic Nanofiltration Membranes: Correlation between Fine Structure and Ultrahigh Permeability. Macromolecules 2013, 46, 2228–2234.

6. Chen, Y.; Liu, F.; Wang, Y.; Lin, H.; Han, L. A Tight Nanofiltration Membrane with Multi-Charged Nanofilms for High Rejection to Concentrated Salts. J. Membr. Sci. 2017, 537, 407–415.
Using Plant Polymethacrylates. Analyst 2019, 144, 799–804.

(23) Hegab, H. M.; ElMekawy, A.; Barclay, T. G.; Michelmore, A.; Zou, L.; Saint, C. P.; Ginic-Markovic, M. Single-Step Assembly of Multifunctional Poly(tannic acid)–Graphene Oxide Coating to Reduce Biofouling of Forward Osmosis Membranes. ACS Appl. Mater. Interfaces 2016, 8, 2581–2588.

(24) Hu, Z.; Berry, R. M.; Pelton, R.; Cranston, E. D. One-Pot Water-Based Hydrophobic Surface Modification of Cellulose Nanocrystals
(44) Yang, H.-C.; Xie, Y.; Hou, J.; Cheetham, A. K.; Chen, V.; Darling, S. B. Janus Membranes: Creating Asymmetry for Energy Efficiency. *Adv. Mater.* 2018, 30, No. 1801495.

(45) Yao, X.; Chen, L.; Ju, J.; Li, C.; Tian, Y.; Jiang, L.; Liu, M. Superhydrophobic Diffusion Barriers for Hydrogels via Confined Interfacial Modification. *Adv. Mater.* 2016, 28, 7383–7389.

(46) Veenu, B.; Dhanaraju, M.; Sonal, G.; Santosh, J.; Bhavana, K.; Yashpal, S. C.; Hardik, C.; Shagun, K.; Kavita, R.; Atul, K.; Mala, S.; Satya, N. S.; Praveen, K. S.; Jagdamba, P. M.; Rabi, S. B.; Mohammad, I. S.; Rajkamal, T.; Gopal, G.; Vishnu, L. S. N-Alkyl/Aryl-4-(3-Substituted-3-Phenylpropyl)Piperazine-1-Carbothioamide as Dual-Action Vaginal Microbicides with Reverse Transcriptase Inhibition. *Eur. J. Med. Chem.* 2015, 101, 640–650.

(47) Tadmor, R.; Pepper, K. G. Interfacial Tension and Spreading Coefficient for Thin Films. *Langmuir* 2008, 24, 3185–3190.

(48) Zhang, P. C.; Zhang, F. L.; Zhao, C. Q.; Wang, S. T.; Liu, M. J.; Jiang, L. Superspreading on Immersed Gel Surfaces for the Confined Synthesis of Thin Polymer Films. *Angew. Chem., Int. Ed.* 2016, 55, 3615–3619.

(49) Khanlari, S.; Marc, A. D. Reaction Monitoring of in situ Formation of Poly (Sodiumacrylate)-Based Nanocomposites Using ATR-FTIR Spectroscopy. *Ind. Eng. Chem. Res.* 2015, 21, 5598–5603.

(50) Koch, C.; Markus, B.; Patrick, W.; Bettina, L.; Maria, R. P.; Stefan, R.; Christoph, H.; Bernhard, L. Ultrasound-Enhanced Attenuated Total Reflection Mid-Infrared Spectroscopy in-Line Probe: Acquisition of Cell Spectra in a Bioreactor. *Anal. Chem.* 2015, 87, 2314–2320.

(51) Ohta, K.; Reikichi, I. Experimental Proof of the Relation between Thickness of the Probed Surface Layer and Absorbance in FT-IR/ATR Spectroscopy. *Appl. Spectrosc.* 1985, 39, 418–425.

(52) Khorshidi, B.; Thundat, T.; Fleck, B. A.; Sadrzadeh, M. A Novel Approach toward Fabrication of High Performance Thin Film Composite Polyamide Membranes. *Sci. Rep.* 2016, 6, No. 22069.

(53) Schaep, J.; Vandecasteele, C. Evaluating the Charge of Nanofiltration Membranes. *J. Membr. Sci.* 2001, 188, 129–136.