Gradient nanoporous phenolics as substrates for high-flux nanofiltration membranes by layer-by-layer assembly of polyelectrolytes

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1. Introduction

Layer-by-layer (LBL) assembly of oppositely charged polyelectrolytes on ultrafiltration (UF) substrates is appealing for preparing thin film composite (TFC) nanofiltration (NF) membranes with high permeances over the past few decades [1]. Polycations and polyanions are alternating sequentially LBL assembled on charged substrates, leading to the formation of thin separation layers [2]. The LBL assembly of polyelectrolytes is dominated by molecular interactions such as electrostatic interaction, hydrogen bonding interaction and covalent bonding interaction [3–5]. The prepared polyelectrolyte NF membranes are endowed with intrinsic surface charges and consequently high separation properties to ions and charged molecules [6–9]. Moreover, because of the easy and highly controllable preparation process, the LBL assembled polyelectrolyte NF membranes have garnered considerable interest in wastewater treatment, desalination, textile and pharmaceutical industries [10–14].

Although tremendous efforts have been put in the studies on the LBL assembled polyelectrolyte NF membranes, high permeance and high selectivity cannot be achieved simultaneously, which is known as the “trade-off” effect [15]. Thinner separation layers obtained by decreasing the number of LBL cycles result in higher permeance, however, the selectivity declines rapidly [16]. Some researchers further studied on tuning outermost assembled layer to improve the selectivity based on the electrostatic interaction mechanism. The desired surface charge was formed by surface modifications for rejecting oppositely charged species, and the charge density can be adjusted to optimize the rejection effects [17,18]. However, the extremely thin separation layers will weaken the mechanical stability of the membranes, which limits their commercial availability. Moreover, the membrane fabrication conditions were tailored to enhance the overall performances of the polyelectrolyte NF membranes [10]. For example, membranes assembled in the solutions with high ion strength exhibited higher protein absorption capacity because the surface roughness of the membranes was significantly enhanced [19,20]. However, the thickness of the membranes was increased due to the enhanced charge screening, leading to the declined permeances. In addition, because of the unprecedented choice of materials including organic, inorganic and biomolecular polyelectrolytes, selection of the right pair of polyelectrolytes is another approach to control the properties of the polyelectrolyte NF membranes [21]. Polyzwitterions, block copolymers, biomasses and other materials
were extensively investigated to fabricate polyelectrolyte NF membranes with good permeselectivities [22,23]. Nevertheless, in some cases, the interactions between assembled polyelectrolytes were weak and an extra cross-linking step was required to ensure the durability of the produced membranes [24]. Moreover, tedious and complicated operations were involved in these methods. Therefore, a simple approach towards polyelectrolyte NF membranes with high permeances, high rejections and good durability requires further exploration.

The TFC structures are consisted of a thin separation layer on top of a porous UF substrate, which provides an alternative way to increase the permeance by optimizing the separation layers and the substrates independently [25]. Unfortunately, researches on tailoring performances of the substrates are sparse [26–28]. Most commonly used UF substrates (such as polysulfone, polyether sulfone, polyacrylonitrile) prepared by the phase inversion processes are suffering from relatively low permeances, inherently limiting the permeance of the polyelectrolyte NF membranes [29,30]. Microfiltration substrates with higher permeances were employed to prepare LBL assembled polyelectrolyte NF membranes with high permeances, however, a sacrificial layer was required to ensure the formation of thin separation layer on the surface of substrates [31,32]. This sacrificial layer needed to be removed, weakening the interactions between the separation layer and the substrate [33]. Basically, LBL assembled polyelectrolyte NF membranes need charged substrates with high permeances but small pores on the surface. However, such substrates were barely explored [34]. Recently, we developed gradient nanoporous phenolics in macroporous polyvinylidene fluoride (PVDF) substrates via fast solvent evaporation at high temperature under hypersaline conditions [35,36]. The prepared gradient phenolic@PVDF membranes exhibited sub-5 nm pores on the surface and high permeances several times higher than other UF membranes with similar rejections. Moreover, the prepared membranes were negatively charged because of the abundant hydroxyl groups, which will induce the electro-static interactions between polyelectrolytes and such membranes. We expect that polyelectrolyte NF membranes with high permeances can be achieved by using such membranes as the substrates.

Herein, such gradient phenolic@PVDF membranes are used as the substrates to fabricate polyelectrolyte NF membranes via the LBL assembly method. Two polymers with opposite charges, polycation polyethylene oxide (PEI) and polyanion poly(acrylic acid) (PAA), are alternately assembled on the negatively charged substrates. The resultant PEI/PAA NF membranes exhibit much higher permeances than NF membranes prepared by other methods. High rejections to negatively charged dyes are simultaneously achieved.

### 2. Experimental

#### 2.1. Materials

Triblock copolymer polyethylene oxide-block-polypropylene oxide-block-polyethylene oxide (PEO1000-PPO70-PEO1000, Mw = 12600, commercially known as F127) was purchased from Sigma-Aldrich. Polyeugenol (37 wt%), H2SO4 (98 wt%), NaOH (≥96%), HCl (93–94 wt%), NaCl (99.5%), KCl (99.5%), K2Cr2O7 (99.5%), and Congo red (CR) were all obtained from local suppliers (Table 1). All chemicals were used without further purification. Deionized water (conductivity: 8–20 μs·cm⁻¹) was used in all the tests.

#### 2.2. Preparation of phenolic@PVDF ultrafiltration membranes

The phenolic@PVDF membranes were prepared by the method described in our previous work [36]. Resol was firstly synthesized by adding 1.05 g 37 wt% formaldehyde to the mixture of 0.61 g phenol and 0.13 g 20 wt% NaOH, followed by stirring at 75 °C for 1 h. After cooling to room temperature, the solution was titrated to pH 7.0 with 0.6 mol·L⁻¹ HCl and vacuum-dried at 45 °C for 2 h. After 15 µL ethanolic solution were dropped onto the surface of the membranes at room temperature. Membranes were instantly heated at 100 °C for 6 h to evaporate ethanol and polymerize resol. After soaking in 98 wt% H2SO4 at 100 °C for 2 h, ZnCl2 and F127 were added to the resol solution. After stirring in an ice bath for 10 h, the homogeneous ethanolic solution with a concentration of 28 wt% was obtained. To prepare the membranes, 150 µL ethanolic solution were dropped onto the surface of PVDF substrates at room temperature. Membranes were instantly heated at 100 °C for 6 h to evaporate ethanol and polymerize resol. After soaking in 98 wt% H2SO4 at 100 °C for 2 h, ZnCl2 and F127 were removed and the gradient phenolic@PVDF membranes were obtained.

#### 2.3. Preparation of PEI/PAA NF membranes

The PEI/PAA NF membranes were prepared by the LBL assembly method on the gradient phenolic@PVDF substrates (Fig. 1). PEI and

### Table 1

<table>
<thead>
<tr>
<th>Generic name</th>
<th>Mw/da</th>
<th>Charge</th>
<th>λmax (nm)</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Congo red (CR)</td>
<td>696.66</td>
<td>Negative</td>
<td>497</td>
<td></td>
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<tr>
<td>Reactive blue 19 (RB19)</td>
<td>626.54</td>
<td>Negative</td>
<td>596</td>
<td></td>
</tr>
<tr>
<td>Acid fusion (AF)</td>
<td>585.54</td>
<td>Negative</td>
<td>546</td>
<td></td>
</tr>
<tr>
<td>Chrome black T (CBT)</td>
<td>461.38</td>
<td>Negative</td>
<td>530</td>
<td></td>
</tr>
<tr>
<td>Acid Orange 7 (AO7)</td>
<td>350.32</td>
<td>Negative</td>
<td>484</td>
<td></td>
</tr>
<tr>
<td>Rhodamine B (Rhb)</td>
<td>479.01</td>
<td>Neutral</td>
<td>554</td>
<td></td>
</tr>
<tr>
<td>Cationic Yellow X-2RL (CYX)</td>
<td>529.50</td>
<td>Positive</td>
<td>431</td>
<td></td>
</tr>
</tbody>
</table>

① λmax: the maximum absorption wavelength.
PAA were separately dissolved in 0.5 mol·L\(^{-1}\) NaCl solutions at a concentration of 2 mg·mL\(^{-1}\). The homogeneous polyelectrolyte solutions were obtained after stirring at 900 r·min\(^{-1}\) for 5 h. The LBL assembly process was performed at room temperature. The negatively charged phenolic@PVDF substrates were firstly soaked in the polycation PEI solution for 30 min to ensure the adequate assembly of PEI on the substrate followed by water rinsing for two times to remove the excess PEI on the surface. The PEI-assembled substrates were subjected to polyanion PAA solution soaking for 5 min for easily manipulating the thickness of the assembly layer, and then water rinsing for two times. Consequently, the PEI/PAA bilayers were assembled on the membrane surface. Then, the assembly of PEI/PAA bilayers was alternately repeated for 2, 3, 4, 5 and 6 cycles (5 min for each soaking process) to fabricate multilayered PEI/PAA NF membranes. Ultimately, membranes with 3, 4, 5, 6 and 7 cycles of PEI/PAA bilayers were fabricated. The resultant membranes are denominated as PEI/PAA-x, where \(x\) represents the number of LBL cycles.

### 2.4. Characterizations

The surface and cross-sectional morphologies of the membranes were observed by a field emission scanning electron microscope (FESEM, Hitachi S4800, Japan) operated at the voltage of 5 kV. Before observations, the samples were sputter-coated with a thin layer of Pd/Pt alloy to enhance their conductivities. To determine the thicknesses of the polyelectrolyte layers, we measured their thicknesses at 10 locations for each sample based on cross-sectional SEM images and the average values were reported. The surface topographies of the membranes were examined by atomic force microscopy (AFM, XE-100, Park Systems). The chemical structures and compositions of the membranes were characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet 8700) in the attenuated total reflection (ATR) mode. The surface charges of the membranes were measured by a SurPASS 3 electrokinetic analyzer (Anton Paar GmbH, Austria) with 1.0 mmol·L\(^{-1}\) KCl solution as electrolyte solution. In the course of the measurements, the zeta potentials of the membranes were recorded at various pH values adjusted with 0.1 mol·L\(^{-1}\) HCl solution and 0.1 mol·L\(^{-1}\) NaOH solution.

### 2.5. Separation tests

The permeances and rejections of the PEI/PAA NF membranes were tested using a filtration cell (Amicon 8003, Millipore Co.) at a stirring speed of 600 r·min\(^{-1}\) and a pressure of 0.1 MPa. The filtration cell has a working volume of 3 mL and an effective membrane area of 0.9 cm\(^2\). Before the permeance tests, membranes were pre-pressed at 0.1MPa for 10 min. The permeance tests were conducted at 1.0 bar for 5 min. Aqueous solutions of various dyes including AO7, CBT, AF, RB19, CR, RhB and CYX with a concentration of 50 ppm were used as the feeds to evaluate the separation performances of the PEI/PAA NF membranes. 10 ml of dye solutions were charged into the filtration cell successively. The initial 2 ml of the filtrate were discarded, and the following 3 ml of the filtrate were collected for the rejection analyses. The absorbance intensities of the peaks at the maximum absorption wavelengths of each dye in the feeds, filtrates and retentates were monitored using an ultraviolet (UV)–vis absorption spectrometer (NanoDrop 2000c, Thermo). The permeances and rejections were calculated by Eqs. (1) and (2), respectively.

\[
P = \frac{V}{t \times A \times \Delta P} \tag{1}
\]

where \(P\) (L·m\(^{-2}\)·h\(^{-1}\)·MPa\(^{-1}\)) is the permeance, \(V\) (L), \(t\) (h), \(A\) (m\(^2\)), and \(\Delta P\) (bar) are the volume of the permeated water, the operation time, the effective membrane area, and the transmembrane pressure, respectively.

\[
R = \frac{1 - I_P/I_F}{100\%} \tag{2}
\]

where \(R\) (%) is the rejection, \(I_P\) and \(I_F\) are the absorbance intensities of dyes in the filtrates and feeds, respectively. All the tests were conducted using at least three membranes and the average values were reported.

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Fig. 1. Schematic illustration of the preparation process for the PEI/PAA NF membranes.
3. Results and Discussion

3.1. Assembly of PEI/PAA on substrates

As shown in Fig. 1, the PEI/PAA NF membranes were prepared on the gradient phenolic@PVDF substrates via the LBL assembly method. The phenolic@PVDF substrates are hydrophilic and negatively charged because of the abundant hydroxyl groups of phenolics, triggering the assembly of polycation PEI through electrostatic adsorption. Afterwards, the polyanion PAA was assembled on the PEI layer also through electrostatic adsorption and the assembly of PEI/PAA bilayers was repeated for a desired number of cycles to prepare multilayered PEI/PAA NF membranes.

The assembly of PEI/PAA on the substrates was firstly investigated by FTIR. As shown in Fig. 2, compared with the spectrum of the pristine substrates, a new peak at 1450 cm\(^{-1}\) appears on the spectra of the membranes after PEI/PAA assembly, which is originated from the bending vibration of the C–N bonds of PEI [37]. In addition, the broad peak centered at 3300 cm\(^{-1}\) is enhanced due to the stretching vibration of the N–H bonds of PEI [7,29,38]. The peak at 1640 cm\(^{-1}\) ascribed to the asymmetric stretching vibration of the C=O bonds of PAA is enhanced, and the peak at 1310 cm\(^{-1}\) attributed to the bending vibration of C–O bonds of PAA is observed in the spectra of the membranes after PEI/PAA assembly [38,39]. Besides, the peaks at 2940 cm\(^{-1}\) and 2840 cm\(^{-1}\) ascribed to the stretching vibrations of \(–\text{CH}_2\) of PEI/PAA are observed [40,41]. The intensities of the above-mentioned peaks are increasing with the increasing number of cycles, suggesting that increasing amount of PEI and PAA are deposited on the substrates after polyelectrolyte soaking. Furthermore, the PEI/PAA NF membranes exhibit a new peak at 1545 cm\(^{-1}\), which is the characteristic adsorption of the C–N bonds from the amide groups and confirms the formation of covalent amide bonds between PEI and PAA [42,43]. These results demonstrate that the deposited PEI and PAA are successfully assembled on the substrates. Consequently, the interactions between PEI/PAA layers are enhanced, ensuring the durability of the PEI/PAA NF membranes and avoiding dissolution of polyelectrolytes in water in a long term.

The assembly of polyelectrolytes on the substrates will influence the surface charges of the membranes. We measured the zeta potentials of the pristine substrates and the PEI/PAA-5 under different pH values to explore their surface charges (Fig. 3). The pristine substrate shows a negative surface charge because of the presence of hydroxyl groups on the surface when pH is higher than their isoelectric point of 3.30. After the assembly of PEI/PAA on the substrate, the PEI/PAA-5 shows an isoelectric point of 5.35. Compared with the pristine substrate, the PEI/PAA-5 exhibits lower negative zeta potentials at pH higher than isoelectric point. These results indicate a weakened negative charge of the PEI/PAA NF membranes than that of the substrate, which is attributed to the introduction of the polycation PEI [44].

3.2. Morphologies of PEI/PAA NF membranes

The surface morphologies of the PEI/PAA NF membranes with different LBL cycles are shown in Fig. 4a–d and Fig. S1a–b. The surface of the pristine phenolic@PVDF substrate is rugged (Fig. 4a). The rugged structure of substrate is covered by a thin PEI/PAA layer and becomes blurred after 3 LBL cycles (Fig. 4b). 4 LBL cycles lead to a smoother surface with a few pits (Fig. 4c). With further increase of the number of LBL cycles, the PEI/PAA-5, -6 and -7 show a compact and smooth surface appearance (Fig. 4d and Fig. S1a–b). This evolution of surface morphologies indicates the increased amount of assembled PEI/PAA with the increase of the number of LBL cycles, which agrees with the FTIR results. Furthermore, we used AFM analyses to characterize the average surface roughness (\(Ra\)) of the pristine substrates and the PEI/PAA NF membranes (Fig. 4i–l). The \(Ra\) of the pristine substrates is 115.1 nm (Fig. 4i). In comparison, the \(Ra\) is greatly decreased to 22.2 nm, 13.9 nm and 3.5 nm for PEI/PAA-3, -4, and -5, respectively (Fig. 4j–l). The \(Ra\) values of the PEI/PAA NF membranes are consistent with their surface morphology. Notably, the substrates were soaked in the solutions of PEI and PAA in the assembly process, resulting in the deposition of PEI and PAA on the bottom surface of the substrates. However, the continuous PEI/PAA layers cannot be formed on the bottom surface which is composed of macropores with pore size > 200 nm (Fig. S2).

The cross-sectional morphologies of the pristine substrates and the PEI/PAA NF membranes were further investigated (Fig. 4e–h and Fig. S1c–d). The thicknesses of the assembled PEI/PAA layers are 170, 260, 430, 610, and 860 nm for the PEI/PAA-3, -4, -5, -6, and -7, respectively. We further analyzed the relationship between the thickness of the PEI/PAA layer and the LBL cycles by linear fitting. As shown in Fig. S3, the coefficient of determination (R-square) of linear fitting is 0.974, indicating that there is a good linear increase in thickness with the increasing LBL cycles. The increased thicknesses confirm the increased amount of the assembled PEI/PAA on the substrates, which is consistent with the change of surface morphologies and the FTIR results. Moreover, the PEI/PAA layers are tightly attached to the substrates because it is electrostatically interacted with the substrates. Some of the polyelectrolyte solution, meanwhile, will imbibe into the substrate.
which also enhanced the adhesion between the bilayer and the substrate, endowing the PEI/PAA NF membranes with good durability.

### 3.3. Separation performances of PEI/PAA NF membranes

We firstly tested the pure water permeances (PWP) of the substrate and the PEI/PAA NF membranes. The gradient phenolic@PVDF substrate showed a high PWP of 11800 L·m$^{-2}$·h$^{-1}$·MPa$^{-1}$. After LBL assembly, the PWP is gradually decreased from 891 to 662, 506, 335 and 291 L·m$^{-2}$·h$^{-1}$·MPa$^{-1}$ for the PEI/PAA-3, -4, -5, -6 and -7, respectively (Fig. 5). The decrease in PWP is due to the increasing thicknesses of the assembled PEI/PAA layers, which increase the mass transfer resistances of the membranes [16]. The rejection rates of the PEI/PAA NF membranes were then investigated using the negatively charged dye, AO7, which can be rejected by the membranes through the electrostatic repulsion mechanism because of the membranes are negatively charged as revealed in Fig. 3. The substrates showed a low rejection of 16.8% to AO7 (Fig. S4), which is greatly improved after LBL assembly. As shown in Fig. 5, the PEI/PAA-3 and -4 can retain 69.8% and 92.0% of AO7, respectively. High rejections over 96.5% to AO7 are achieved for the PEI/PAA-5, -6 and -7. Moreover, as shown in Fig. S5a, the absorbance intensity of the retentate is higher than that of the feed, implying that adsorption plays a negligible role in the rejection of AO7 [45]. With the increase of the number of LBL cycles, the thicknesses of the separation layer are gradually increased, leading to the increased rejections to AO7. The assembled PEI/PAA layers with more than 5 LBL cycles are continuous and compact, resulting in the high rejections to AO7.

Considering that the PEI/PAA NF membranes are negatively charged, we expect that they may show high rejection rates to other negatively charged solutes due to the electrostatic repulsion. We tested the rejection rates of the PEI/PAA-5 to other negatively charged dye molecules including CBT, AF, RB19 and CR. After rejection tests, all the filtrates of the above dyes are transparent whereas the retentates exhibit darker colors than the feeds (insets in Fig. 6). The retentates show higher absorbance intensities than the feeds in the UV–vis spectra, indicating the rejection effect plays a dominating role in the dyes separation process. (Fig. S5b–e). The rejection rates to CBT, AF, RB19 and CR of the PEI/PAA-5 are 99.1%, 96.1%, 99.7% and 99.7%, respectively (Fig. 6). The increase in rejections is mainly due to the successively increased molecular weights of AO7, CBT, RB19 and CR (Table 1 and Fig. 6). Notably, similar rejections to AO7 and AF are determined although AO7 has a smaller molecular weight than AF. However, the molecular size of AO7
is 1.28 nm × 0.78 nm, which is larger than that of AF (1.17 nm × 1.13 nm). The long axis of AO7 molecules might partly enhance the rejection. Therefore, the molecular weight and molecular size synergistically influence the rejection processes in addition to the electrostatic repulsion.

We further tested the rejections of the PEI/PAA-5 to positively charged CYX and neutrally charged RhB. Static adsorptions were firstly performed to minimize the effect of adsorption on rejection before the rejection tests [46]. Membranes were immersed into CYX and RhB solutions with a concentration of 100 ppm for 24 h, respectively. The color of CYX and RhB solutions becomes lighter after adsorption for 24 h (insets in Fig. 7a–b). The UV–vis absorption spectra of the dye solutions before and after adsorption tests are presented in Fig. 7a–b. The solutions after adsorption tests exhibit lower absorbance intensities than the original solutions, suggesting that CYX and RhB molecules are distinctly adsorbed by the PEI/PAA-5. According to the absorbance intensities of the maximum absorption peaks, 78.0% CYX molecules and 14.7% RhB molecules were adsorbed by the PEI/PAA-5, respectively [31]. After static adsorption treatments, membranes were washed with water and then used to test the rejection of the same dye. The rejection to CYX of the PEI/PAA-5 is 97.9% (Fig. 7c). However, the absorbance intensity of the retentate is lower than that of the feed, implying that the electrostatic adsorption still takes places although the membrane has been subjected to adsorption pretreatment, and plays a dominant role in rejecting positively charged dyes. Fig. 7d reveals that the rejection to RhB of the PEI/PAA-5 is 61.3%. The retentate shows a higher absorbance intensity than the feed, implying that negligible adsorption of RhB happens. Therefore, it is clarified that the PEI/PAA NF membranes retain neutrally charged dyes mainly by the size discrimination effect. One may argue that membranes with PEI as the outermost interface may retain positively charged dyes by the electrostatic repulsion mechanism. We fabricated the PEI/PAA-4.5, which was concluded with PEI, and tested its
rejection to positively charged CYX. As shown in Fig. S6, the membrane still has a strong adsorption for positively charged dyes.

We compared the separation performances of the PEI/PAA NF membranes with those of membranes prepared by other methods. As shown in Fig. 8, most reported membranes presented moderate PWP of \(<200 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}\) when they exhibited high rejections to AO7 and AF of \(>90\%\). In this work, a PWP of \(\sim 500 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}\) with comparable rejections to AO7 and AF can be achieved, which is \(\sim 2–10\) times higher than previously reported values. Such a high permeance is attributed to the highly permeable substrates, verifying the importance of the substrates for the improvement in separation performances of the produced NF membranes. In summary, the success in the preparation of high-flux NF membranes using the gradient phenolic/PVDF substrates in the present work should be attributed to the unique structural features of the substrates including 1) high permeability allowing water to pass with low resistance, 2) tight surface with sub-5 nm pores enabling polyelectrolytes to form thin but compact covering layer to deliver the NF function, and 3) the presence of rich hydroxyl groups on the surface ensuring tight deposition of oppositely charged polyelectrolytes to form durable selective layers.

**Fig. 8.** Comparison of the separation performances of the PEI/PAA NF membranes with other membranes in terms of rejections to AO7 (orange symbols) and AF (violet symbols), and PWP. The detailed data are listed in Table S1.

### 4. Conclusions

In this work, high-flux NF membranes are prepared via the LBL assembly method by using gradient phenolic/PVDF ultrafiltration membranes with high permselectivity as substrates. Polycation PEI and polyanion PAA are LBL assembled on the surface of the negatively charged phenolic substrates initiated by the electrostatic interactions, leading to the formation of thin PEI/PAA layers tightly attached to the substrates. Moreover, PEI and PAA are interacted by electrostatic interactions and covalent bonds, ensuring the durability of the membranes. The PEI/PAA NF membranes prepared with 5 LBL cycles represent a superior permeance of \(506 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}\), which is \(\sim 2–10\) times higher than membranes prepared by other methods. High rejections of \(\sim 96\%\) to different negatively charged dyes are meanwhile achieved due to the negative nature of the produced membranes. Moreover, high rejections to positively charged dye molecules because of the electrostatic adsorption mechanism are revealed. Moderate rejections to neutrally charged dye molecules can also be realized by size discrimination. This work demonstrates a new approach to high-flux NF membranes, which is expected to extend to upgrade the permeability of other thin-film composite membranes.

### Supplementary Material

Supplementary data to this article can be found online at [https://doi.org/10.1016/j.cjche.2019.04.011](https://doi.org/10.1016/j.cjche.2019.04.011).

### References


