Supporting Information

Nanofilms Directly Formed on Macro-Porous Substrates for Molecular and Ionic Sieving

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Experimental Section

Materials

Dopamine hydrochloride was procured from Sigma-Aldrich. Polyethyleneimine (PEI, Mw=600 Da), pyrogallic (PG), diethylenetriamine (DETA), triethylenetetramine (TETA), and dyes including Orange II, Methyl blue, Methylene blue, Rhodamine B, Direct red 80, Azure B, Evans blue and Methyl orange were obtained from Aladdin Chemical Co. Ltd (China). Polypropylene microfiltration membranes were purchased from Membrana GmbH (Germany) and used as hydrophobic macroporous substrates. The mean pore size is about 0.2 μm with a porosity of 75%. These substrates were cut into rounds with a diameter of 47 mm and rinsed by acetone under oscillation overnight. Then, they were dried in a vacuum oven overnight. Other reagents such as catechol (CCh), glutaraldehyde, diethylene glycol, triglycol, polyethylene glycol and ethanol were obtained from Chemical Reagent Co., Ltd. All the reagents were used directly.

Fabrication of the phenols/amines nanofilms

Dopamine and PEI were dissolved in Tris-buffer solution (200 mM, pH=8.5) at a designed mass ratio. The concentration of dopamine was fixed at 2 mg/mL. The substrates were floated on the fresh prepared dopamine/PEI solution for 2 h to 8 h, and then rinsed in deionized water. The nanofilms were immersed in a 2.5% glutaraldehyde solution under 50 °C for 20 min for further cross-linking, and post-treated in an oven under 50 °C for 20 min. The as-prepared nanofilms were washed by deionized water and reserved in the water for following filtration. To accelerate the deposition, the nanofilm and solution were settled

under an oxygen atmosphere for 20 min to 2 h, or reacted at a relatively high temperature (55 °C-85 °C) for 10-20 min.

For other phenol/amine nanofilms, phenols/amines were dissolved in same Tris-buffer solution with a concentration of 2 mg/mL respectively. The substrate and solution were settled under an oxygen atmosphere for 0.5 h. Then, nanofims were immersed in a 2.5% glutaraldehyde solution under 50 °C for 20 min, followed by post-treatment in an oven under 50 °C for 20 min. The as-prepared films were washed by deionized water and reserved in the water for following characterization and test.

Characterization

The surface morphologies of nanofilms were observed by field emission scanning electron microscopy (FESEM, Hitachi, S4800, Japan) and the surface chemistries were revealed by X-ray photoelectron spectroscopy (PerkinElmer, USA). The water contact angles were detected by a contact angle system (MAIST Vision Inspection & Measurement Co. Ltd., DropMeter A-200, China). The surface potential was measured based on a streaming potential method by an electrokinetic analyzer (SurPASS Anton Paar, GmbH, Austria). The electrolyte solution is KCl solution with a concentration of 1 mmol/L, and the pH was adjusted by 0.1 mol/L NaOH and HCl solutions during the measurement.

Separation performance evaluation

The separation performance was evaluated in a cross-flow flat module with an effective area of 7.07 cm^2. The feed solutions were prepared by dissolving various dyes and salts into the deionized water. The concentration of dyed solution is 0.1 g/L while the concentration of the saline solution is 1 g/L. Before the test, the nanofilms were pre-wetted by a mixture of ethanol/water (the volume ratio is 6:4). Then, the nanofilms were pre-compacted under 0.8 MPa for 1 h until the stable flux and rejection. The filtration experiments were operated under 0.6 MPa at 25 °C. The water flux was calculated by the following equation (**Eq. S1**):

$$F = \frac{Q}{A \cdot t} \quad \textbf{(Eq. S1)}$$

where Q is the detected water flux, A is the effective area and t is the permeation time. The rejection was calculated by **Eq. S2**:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad \textbf{(Eq. S2)}$$

where C_p and C_f represent the salt concentration of permeate and feed, respectively. The concentrations of dyes in water were measured by an ultraviolet spectrophotometer (UV 2450, Shimadzu, Japan). The concentration of the salt solution was detected by an electrical conductivity meter (Mettler Toledo, FE30, Switzerland). For molecular weight cutoff measurement (MWCO), a series of electroneutral solutes (ethylene glycol, diethylene glycol, triglycol and polyethylene glycol) with different molecular weights (62, 106, 150, 200 and 2000 Da) were used as electroneutral solutes to detect the MWCO of the nanofilms.

Calculation of surface adhesion work

The surface adhesion work of PDA/PEI nanofilm on polymer substrates can be calculated according to the following equation:

$$W_{wos} = 2\left[\gamma_w^d + \gamma_w^p + \sqrt{\gamma_s^d \gamma_o^d} + \sqrt{\gamma_s^p \gamma_o^p} - \sqrt{\gamma_s^d \gamma_w^d} - \sqrt{\gamma_s^p \gamma_w^p} - \sqrt{\gamma_o^d \gamma_w^d} - \sqrt{\gamma_o^p \gamma_w^p}\right] \quad \textbf{(Eq. S3)}$$

where r_w^d, r_s^d, r_f^d are the nonpolar components of surface tension for water, substrate and film, and r_w^p, r_s^p, r_f^p are the polar components correspondingly.

To obtain the r_f^d and r_f^p, we detected the contact angles of water and diiodomethane on the free-standing PDA/PEI nanofilm surface prepared as described in our previous work (*RSC Adv.*, **2014**, 4, 45415). The PDA/PEI surface towards air is very smooth. Therefore, the surface can be regarded as an ideal smooth and flat surface. The measured contact angles are $\theta(H_2O) = 64°$ and $\theta(CH_2I_2) = 47°$, and r_f^d and r_f^p can be calculated as follows:

$$\cos\theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} \quad \textbf{(Eq. S4)}$$

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^d \gamma_l^d} - 2\sqrt{\gamma_s^p \gamma_l^p} \quad \textbf{(Eq. S5)}$$

$$\cos\theta = -1 + 2\left(\frac{\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p}}{\gamma_l}\right) \quad \textbf{(Eq. S6)}$$

Finally we obtained $\gamma_f^d = 27.20\ mJ/m^2, \gamma_f^p = 14.52\ mJ/m^2$, and **Equ. S3** can be converted to **Eq. S7**:

$$W_{wos} = 1.51\sqrt{\gamma_s^d} - 6.83\sqrt{\gamma_s^p} + 42.6 \quad \textbf{(Eq. S7)}$$

Detailed discussion about the effects of solution composition on nanofilm performance

The solution composition has complicated effects on film structure and final separation performance. Therefore, we investigated the influences of solution composition, including polyphenol/polyamine ratio, initial concentration and combination, on structure and sieving capacity of the nanofilms fabricated under ambient conditions. The nanofilms showed a good rejection to divalent cations such as Ca^{2+} and Mg^{2+}, which can be rationalized by the highly positively charged surface of the nanofilms originated from the rich amino groups in polyamines. We measured the Zeta potential of the PDA/PEI films with an initial DA/PEI ratio of 1:1, which is around 30 mV under the filtration conditions (**Figure S12**). Therefore, the $MgCl_2$ solution was selected as the feed solution to evaluate the ion rejection of nanofilms in our experiments. Before investigating the effects of solution composition, we identified the optimal reaction time for film fabrication (**Figure S15a**). For the solution with a DA/PEI ratio of 1:1, the $MgCl_2$ rejection was promoted from 56.3 ± 13.7% to 92.6 ± 1.5% when the reaction time increased from 2 h to 8 h, with the decrease of permeate flux accordingly. More specifically, the salt rejection was significantly improved at the early stage, while it changed slightly but with dramatically flux decrease after 6 h, caused by the

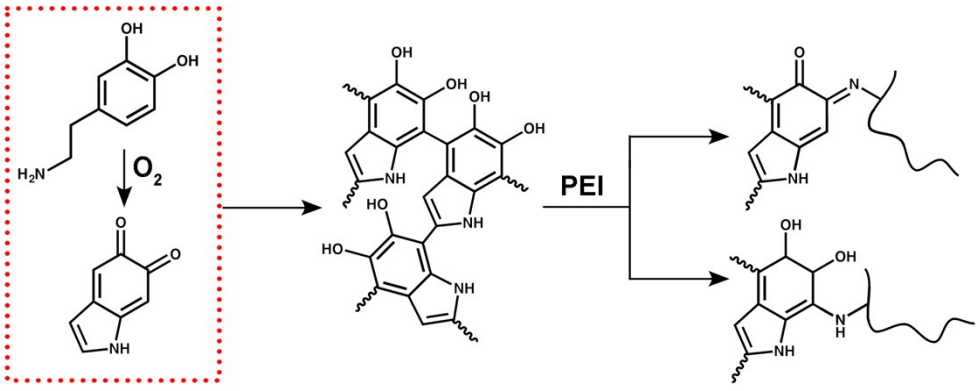
rapid growth of film at the following stage arising from the large particle aggregation. As a result, we selected 6 h as a proper reaction time under air atmosphere and room temperature. Then we investigated the effects of DA/PEI ratio on nano film structure and performance (**Figure S15b**). Both high and low DA/PEI ratios result in a salt rejection lower than 80%. The nanofilm with a DA/PEI ratio of 4:1 is thick but with loose particle-packing structure, leading to the undesirable decrease in both water permeation flux and salt rejection. On the other hand, the nanofilm is too thin to reject the ions when the DA/PEI ratio is 1:2 in the solution. Moreover, the big error bars also indicate the low reproducibility of the films under this condition. The maximum $MgCl_2$ rejection above 90% is achieved at a DA/PEI ratio of 1:1, along with a high permeate flux near 80 $Lm^{-2}h^{-1}$ under 0.6 MPa. The initial DA and PEI concentration also influences the film performance (**Figure S15c**). The rejection increases to 94.1 ± 0.7% with doubled concentration, while the permeate flux decrease to only 23.2 ± 1.0 $Lm^{-2}h^{-1}$ as expected. Further increase in concentration leads to a dramatic flux decrease but negligible rejection promotion. These results are ascribed to both the thickness and density increase in the nanofilms. Based on these results, we selected the DA/PEI ratio of 1:1 and initial concentration of 2 mg/mL as the fabrication parameters in the following experiments. It should be mentioned the nanofilms prepared by other polyphenol/polyamine combinations show significant differences in separation performance, which can be optimized in future study to satisfy the requirements of different sieving processes (**Figure S16**).

Table S1 Adhesion work of PDA/PEI film on different polymer material surfaces.

Materials	γ_s^d (mJ/m^2)	γ_s^p (mJ/m^2)	W_{aos} (mJ/m^2)	W_{wos} (mJ/m^2)
PP	27	0.1	56.61	48.29
PVDF	23.2	7.1	70.54	31.68
PTFE	17	0.6	48.91	43.54
PS	41.4	0.6	48.91	47.05
PE	30	1.3	65.82	43.08

Table S2 Thickness and performance of nanofilms fabricated under different temperatures.

Temperature (°C)	Reaction time (min)	Thickness (nm)	Permeate flux (Lm^{-2}h^{-1})	$MgCl_2$ Rejection (%)
55	**20**	**26.49±4.26**	**101.96±5.23**	**91.52±2.12**
55	30	57.07±3.50	58.65±4.33	91.02±1.23
55	40	76.41±5.55	28.48±2.12	86.21±3.23
70	10	14.62±1.77	136.03±3.56	76.10±4.45
70	**15**	**21.26±1.46**	**86.36±4.68**	**94.56±0.96**
70	20	57.27±11.08	39.94±1.53	94.12±1.32
85	5	10.89±1.02	246.86±10.14	24.00±1.34
85	**10**	**13.87±1.04**	**105.66±18.30**	**93.40±1.01**
85	15	18.42±1.76	37.28±2.54	83.19±5.24



Scheme S1 The reaction mechanisms between DA and PEI.

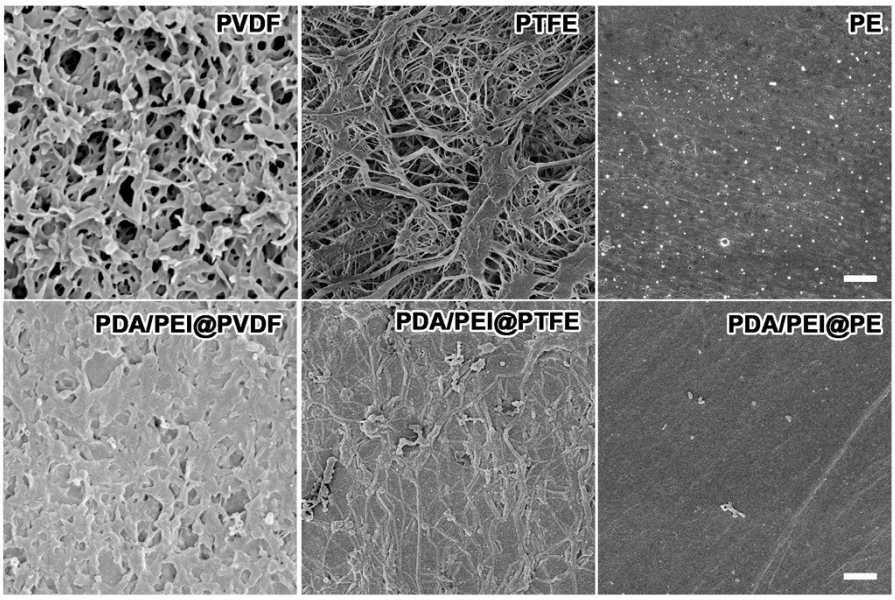


Figure S1 SEM images of PVDF, PTFE and PE substrates and the PDA/PEI nanofilms on them. The scale bar is 1 μm.

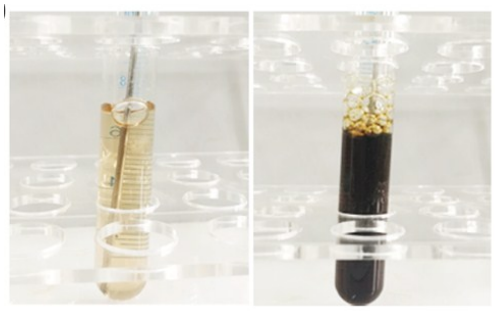


Figure S2 Bubbling through DA/PEI solution after reacting 10 min (left) and 4 h (right).

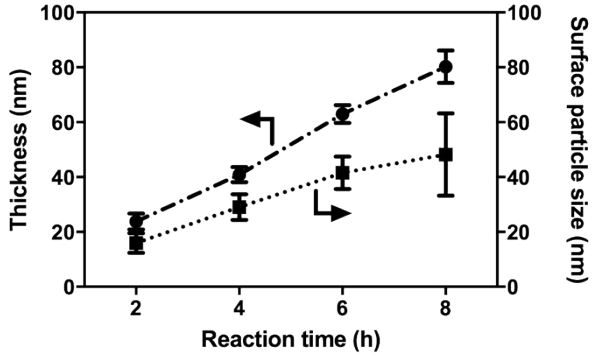


Figure S3 The thickness and surface particle size of nanofilm with the time. The DA/PEI ratio in solution is 1:1.

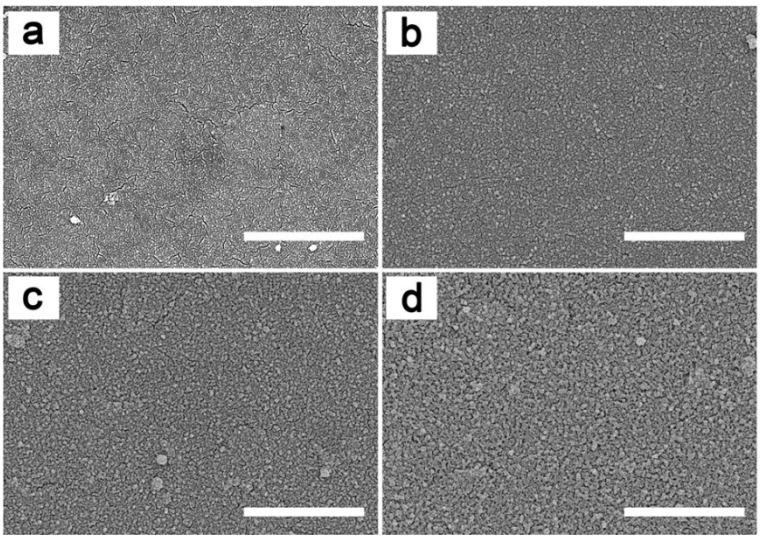


Figure S4 Surface morphologies of PDA/PEI nanofilms with different reaction time: a) 2 h, b) 4 h, c) 6 h and d) 8 h. The DA/PEI ratio is 1:1 and the scale bar is 2 μm.

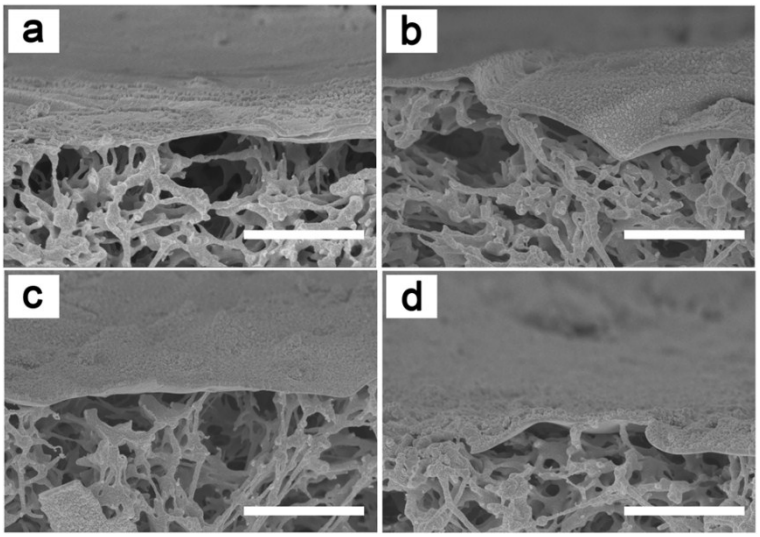


Figure S5 Cross-section morphologies of PDA/PEI nanofilms with different reaction times: a) 2 h, b) 4 h, c) 6 h and d) 8 h. The DA/PEI ratio is 1:1 and the scale bar is 2 μm.

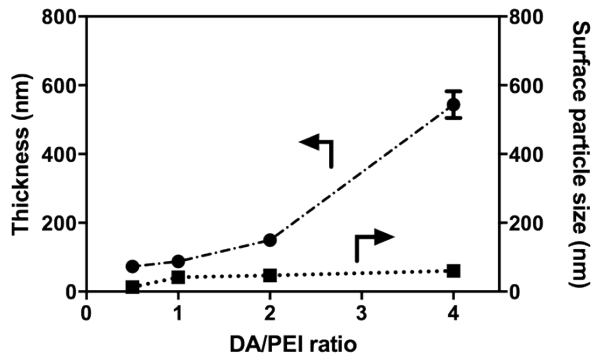


Figure S6 The thickness and surface particle size of nanofilm with different DA/PEI ratios. The deposition time is 6 h.

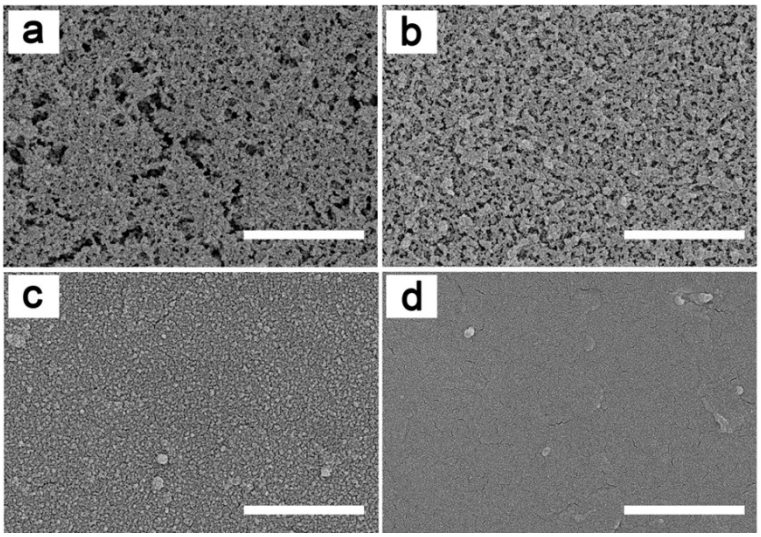


Figure S7 Surface morphologies of PDA/PEI nanofilms with different DA/PEI ratios: a) 4:1, b) 2:1, c) 1:1 and d) 1:2. The reaction time is 6 h and the scale bar is 2 μm.

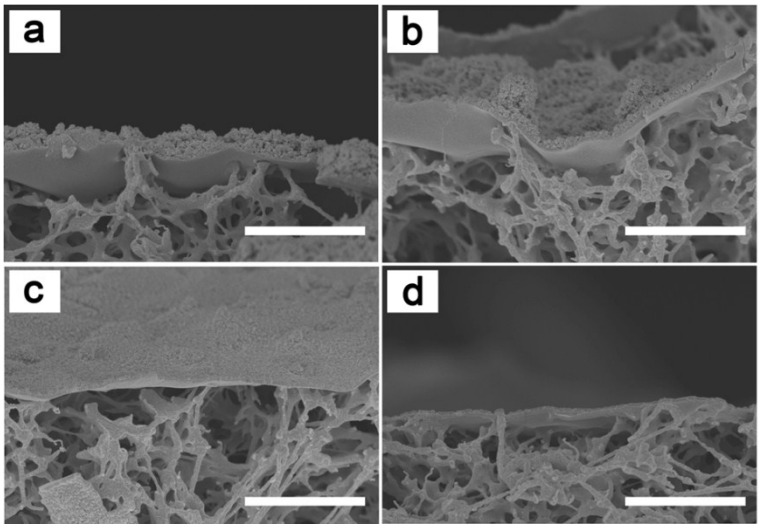


Figure S8 Cross-section morphologies of PDA/PEI nanofilms with different DA/PEI ratios: a) 4:1, b) 2:1, c) 1:1 and d) 1:2. The reaction time is 6 h and the scale bar is 2 μm.

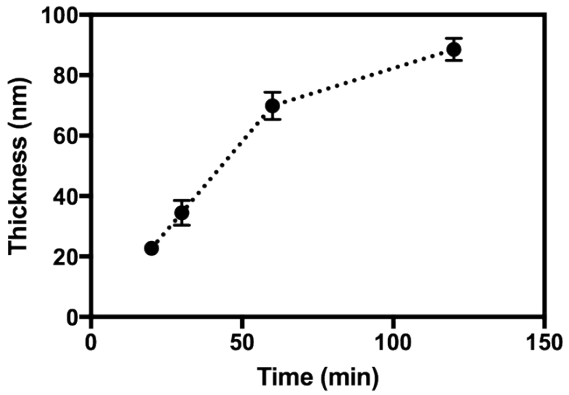


Figure S10 Thickness of nanofilm fabricated under oxygen atmosphere.

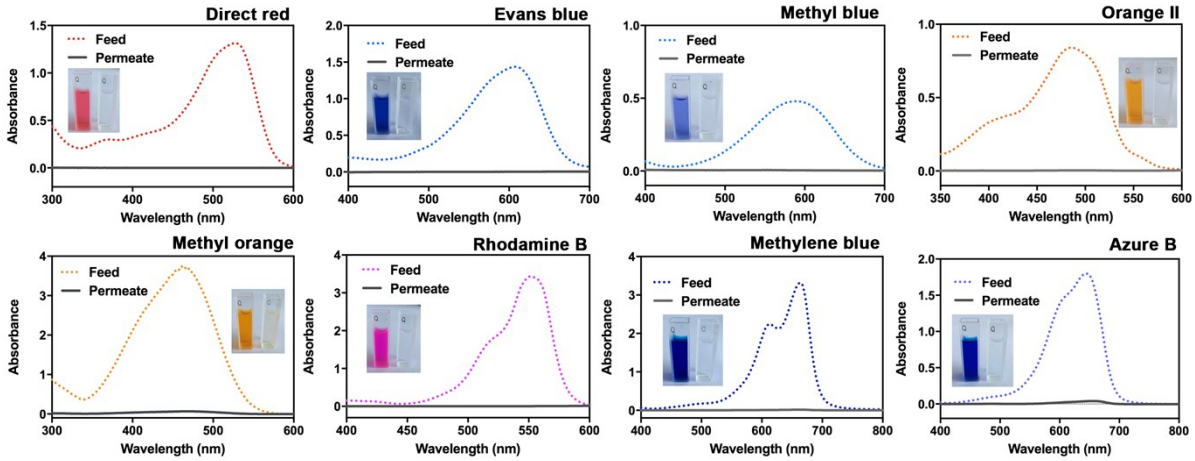


Figure S11 Separation performance of the nanofilms to different dye solutions measured by UV-vis spectra.

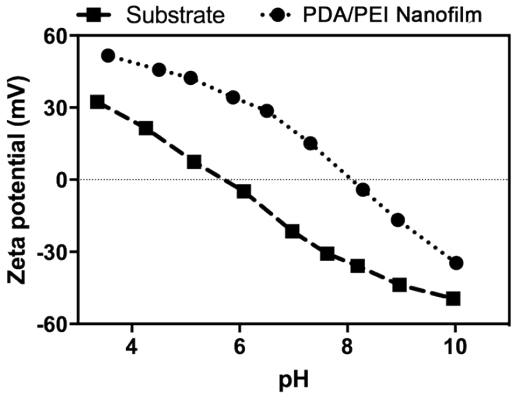


Figure S12 Zeta potential of the substrate and nanofilm surfaces. The substrate is slightly negatively charged while the nanofilm is positively charged in saline solutions.

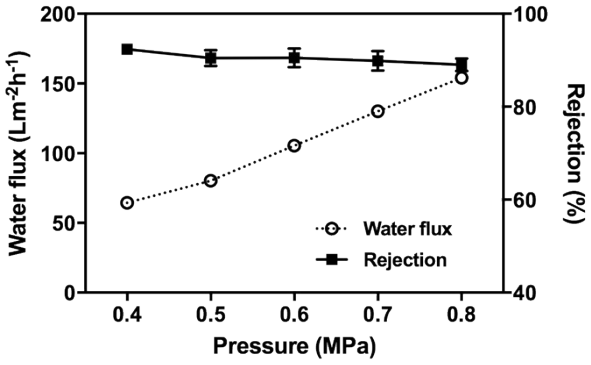


Figure S13 Separation performance of the nanofilms fabricated at 85 °C for 10 min with increased operating pressure.

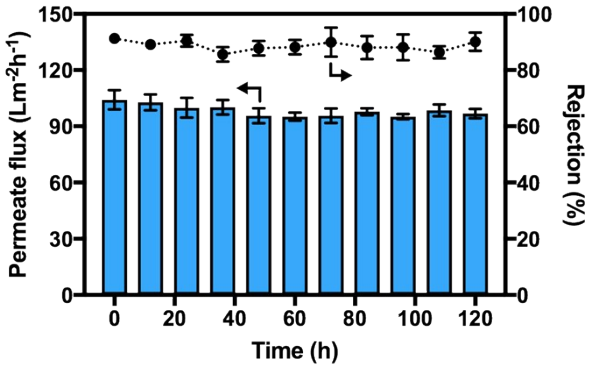


Figure S14 Structure stability of the nanofilms fabricated at 85 °C for 10 min during long-term operation.

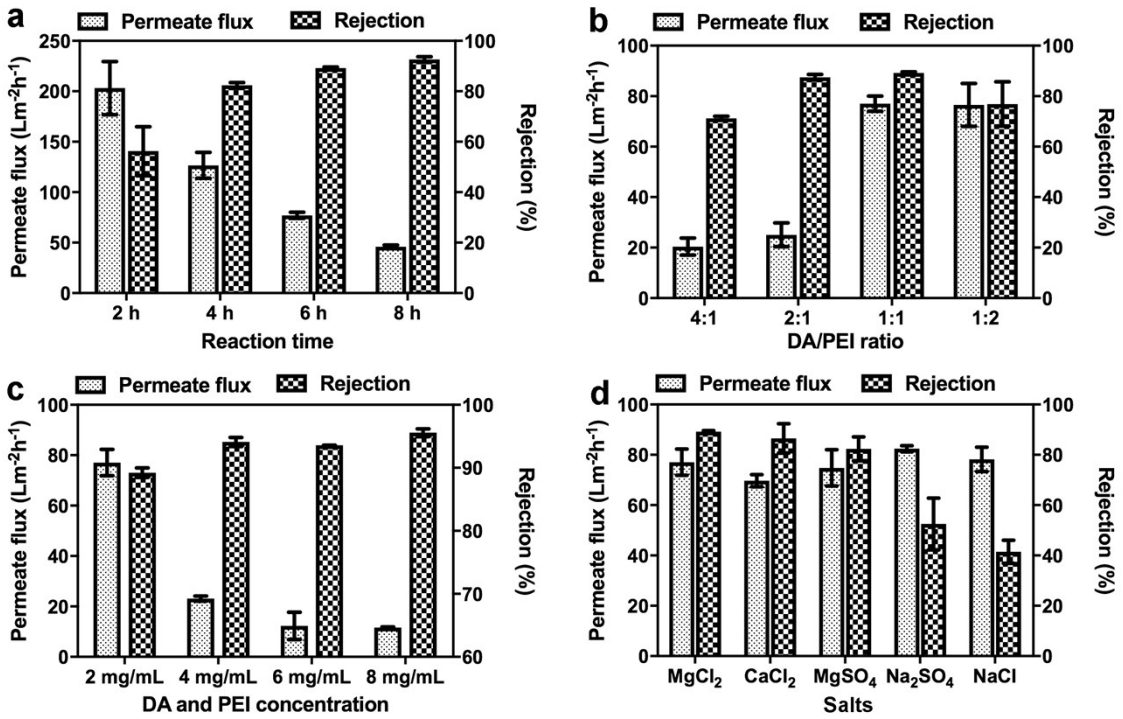


Figure S15 Permeate flux and rejection of the PDA/PEI nanofilms fabricated with different a) reaction times, b) DA/PEI ratios and c) initial concentrations. d) Separation performance of the nanofilms (DA/PEI=1:1, 6 h) for different saline feeds with a concentration of 1 g/L.

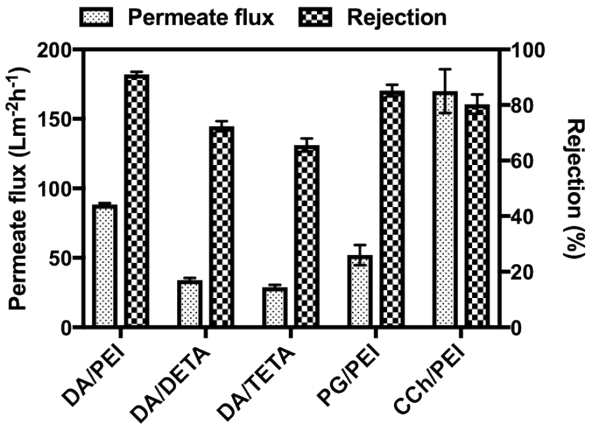


Figure S16 Permeate flux and rejection to $MgCl_2$ solution for polyphenol/polyamine nanofilms with different combinations.