

Electronic Supplementary Information

Nanofiltration Membranes with Narrowed Pore Size Distribution via Pore Wall Modification

Yong Du^a, Yan Lv^a, Wen-Ze Qiu^a, Jian Wu^b, Zhi-Kang Xu^{a*}

^a*MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer
Science and Engineering, Zhejiang University, Hangzhou, 310027, China. E-mail: xuzk@zju.edu.cn.*

^b*Department of Chemistry, Zhejiang University, Hangzhou, 310027, China.*

* Corresponding author. E-mail: xuzk@zju.edu.cn; fax: + 86 571 8795 1773.

1. Experimental

2.1. Materials

Polyacrylonitrile (PAN) ultrafiltration membranes with pore size ranging from 40 to 80 nm (MWCO = 10~30 kDa) were obtained from Shanghai MegaVision Membrane Engineering & Technology Co. Ltd (China). Dopamine hydrochloride, 5,5'-dithio-bis-(nitrobenzoic acid) (DTNB, Ellman's reagent) and SMPS were purchased from Sigma-Aldrich (USA). Polyethyleneimine (PEI, Mw = 600 Da) was purchased from Aladdin (China). Other chemicals, including tris (hydroxymethyl) aminomethane (Tris), hydrochloric acid solution (18 mol/L), sodium hydroxide, chemicals with the formula H-(O-CH₂CH₂)_n-OH, which is called here EG (n = 1), DEG (n = 2), TEG (n = 3), polyethylene glycol with the molecular weight of 200 (PEG200), 400 (PEG400), 600 (PEG600), and inorganic salts, were procured from Sinopharm Chemical Reagent Co. Ltd (China). All of the chemicals were used as received without further purification. Ultrapure water (18.2 MΩ) was produced from an ELGA Lab Water system (France).

2.2. Hydrated radius measurement

The calculation of MPSI hydrated radius was achieved based on Stokes' pioneering work,^{S1} with an electrical conductivity meter (METTLER TOLEDO, FE30, China). The hydrated radius of ion B, r_B can be expressed as:

$$r_B = \frac{0.820|z|}{\lambda_B^0 \eta^0} \quad (1)$$

$$\lambda_{AB}^0 = \lambda_A^0 + \lambda_B^0 \quad (2)$$

where z represents the charge number, η^0 is the viscosity of water, λ^0_A , λ^0_B , λ^0_{AB} are the limiting molar conductivity of ion A, B and the electrolyte as a whole, respectively. $\lambda^0_{Na^+} = 50.10 \text{ cm}^2\Omega^{-1}\text{equiv.}^{-1}$.^{S1} The limiting molar conductivity of SMPS can be obtained as the intercept by linear fitting the molar conductivity of SMPS aqueous solution, Λ_{MSMPS} to the square root of concentration, $c^{0.5}$ as follows:

$$\Lambda_{MSMPS} = \Lambda^0_{MSMPS} - k\sqrt{c} \quad (3)$$

where k is a constant related to the ion species and the test environment.

2.3. Membrane fabrication

PDA/PEI co-deposition NFMs are fabricated according to our previous study.²⁴ PAN ultrafiltration membranes were hydrolyzed at first in 1.5 M sodium hydroxide solution for 1 h at 50 °C, and then immersed into 1 M hydrochloric acid solution for 1 h at room temperature for protonation. The hydrolyzed PAN (HPAN) membranes were washed with ultrapure water for several times and then used as support for the composite NFMs. PEI (1 mg/mL) and dopamine hydrochloride (2 mg/mL) were dissolved in Tris-HCl buffer solution (pH = 8.5, 50 mM). The circular pieces of HPAN membranes with diameter of 5 cm were put into the freshly prepared dopamine/PEI solution and shaken in air at 25 °C for 3 h. The PDA/PEI co-deposition NFMs were washed with ultrapure water for several times. Then the as-prepared NFMs were subjected to a normal nanofiltration process with 2000 mg/L SMPS aqueous solution as feed using a laboratory scale cross-flow flat membrane module at 30 °C under 0.6 MPa for a certain time (typically 12 h) with the permeate solution led back to the feed to keep the thiol concentration as constant. This process can be

monitored by identifying the water permeation and the thiol rejection in real time to obtain the optimized fabrication condition. The water flux can be measured directly by the cross-flow flat membrane module. Water flux (F_w , L/m²h) was calculated according to the following equation:

$$F_w = \frac{Q}{t \cdot A} \quad (4)$$

where Q , t and A represent the volume of permeated water, the permeation time, and the effective membrane area, respectively. Thiol concentrations were measured according to Ellman's method.^{S2} 0.1 mL of permeate or feed solution was added to 0.2 mL 0.01 M DTNB phosphate buffer (pH = 8.0). The mixed solution was diluted to 3 mL after incubated at room temperature for 15 min and subjected to a colorimetric test at 412 nm using an ultraviolet spectrophotometer (UV 2450, Shimadzu, Japan). The thiol rejection can be obtained as follows:

$$R_{thiol} = \left(1 - \frac{A_p - A_0}{A_f - A_0} \right) \times 100\% \quad (5)$$

where A_p and A_f are the absorbance of the permeate and feed solution treated as mentioned above, respectively. A_0 is the absorbance of ultrapure water treated as the same. We also prepared NFMs by incubating PDA/PEI co-deposition membranes in 2000 mg/L SMPS aqueous solution at room temperature for 24 h, for comparison. All of the prepared NFMs were rinsed by ultrapure water for several times and stored in it for further characterization and evaluation.

2.4. Membrane characterization

The surface chemical structures of NFMs were studied by Fourier transform infrared spectrometer (FTIR/ATR Nicolet 6700). The spectra were collected from 400 cm^{-1} to 4000 cm^{-1} by cumulating 32 scans at a resolution of 4 cm^{-1} . More details in atomic components were analyzed by X-ray photoelectron spectrometer (XPS, PerkinElmer, USA) using Al K_{α} excitation radiation (1486.6 eV). The whole spectra were collected ranging from 0 to 1000 eV with a 10-nm survey depth. Static water contact angles (WCA) were measured with a DropMeter A-200 contact angle system (MAIST VisionInspection & Measurement Co. Ltd, China) at room temperature. Each droplet was kept on the sample surface for 15 s before measurement. Surface morphologies of the NFMs were observed with field emission scanning electron microscopy (FESEM, Hitachi, S4800, Japan). A streaming potential method was adapted to detect the charging properties of the NFM surfaces using an electro kinetic analyzer (SurPASS Anton Paar, GmbH, Austria) with 1 mM KCl solution as electrolyte solution.

2.5. Measurement of NFM pore size distribution

Evaluation of the NFM pore size distribution was achieved based on G.-Martín and coworkers' study,²⁸ using a pore-flow model. Briefly, EG, DEG, TEG, PEG200, PEG400 and PEG600 were used as solutes. The observed retention can be expressed as:

$$R_0 = \left(1 - \frac{C_{p0}}{C_{f0}} \right) \times 100\% \quad (6)$$

where C_{p0} and C_{f0} are the solute concentrations in permeate and feed, respectively. The

relationship between R_0 , true retention (R_t), water permeation (J_v) and cross flow rate (ω) can be expressed as follows:

$$\ln\left(\frac{1 - R_0}{R_0}\right) = \ln\left(\frac{1 - R_t}{R_t}\right) + \frac{1}{A} \left(\frac{J_v}{\omega^\alpha}\right) \quad (7)$$

where A is a constant only related to the cross-flow flat membrane module, α is a parameter that depends on the configuration of the experimental setup. R_0 and constant A can be determined by linear fitting $\ln((1-R_0)/R_0)$ to J_v/ω^α .

The geometric standard deviation (GSD) of the pore size, σ_g can be derived with the following equation:

$$\sigma_g = e^{\sqrt{\frac{\sum_{i=1}^n p_i (\ln \frac{A_i}{A_a})^2}{\sum_{i=1}^n p_i}}}$$
(8)

where p_i is the proportion of the pores with radius A_i , A_a is the number average radius of the pores.

2.6. Nanofiltration performance of the NFMs

The nanofiltration performance of the NFMs was evaluated using a laboratory scale cross-flow flat membrane module under 0.6 MPa at 30 °C with the effective area of 7.07 cm² for each sample. Each sample was pre-compacted under 0.6 MPa for 2 h before performance evaluation. Various salt solutions including MgCl₂, CaCl₂, MgSO₄, Na₂SO₄ and NaCl, or mixed salts with Na₂SO₄/NaCl mass ratio = 2:1 at concentration of 1000 mg/L were used as feed solutions with a fixed cross-flow rate of 30 L/h. Stability test was also conducted under the same condition, using Na₂SO₄ as solute in a long-term operation

process of 5 days. Water flux (F_w , L/m²h) was calculated according to equation (4) and solute rejection was calculated as follows:

$$R = \left(1 - \frac{C_p}{C_f} \right) \times 100\% \quad (9)$$

where C_p and C_f are the solute concentrations in permeate and feed, respectively, which was detected by an electrical conductivity meter (METTLER TOLEDO, FE30, China). The concentrations of Cl^- and SO_4^{2-} in mixed solutions are determined by ion chromatography, performed by Science Standards Testing Research Institute (China). All results presented were average values obtained from at least three different membranes prepared under the same condition.

Selectivity of solute A to solute B, α_B^A , is defined the same as previous report.²⁹

$$\alpha_B^A = \frac{100 - R_A}{100 - R_B} \quad (10)$$

where R_A and R_B represent the retention of solute A and solute B, respectively.

Table S1. Surface chemical composition of the PDA/PEI co-deposition NFMs and the NFMs after reacting with SMPS in a nanofiltration flat membrane module for different time from XPS spectra (in atomic percent).

Membrane fabricated for different reaction time (h)	Surface elemental composition (mol%)			
	C	O	N	S
0	69.29	16.05	14.62	0.04
4	68.24	16.85	14.45	0.46
8	68.33	16.44	14.58	0.65
12	68.06	16.27	14.90	0.77

Table S2. Hydrated radius of various ions.

Ions	Hydrated radius
MPSI	0.257 ± 0.002^a
Na ⁺	0.183 ^b , 0.178 ^c
Mg ²⁺	0.346 ^b , 0.300 ^c
Ca ²⁺	0.309 ^b , 0.260 ^c
Cl ⁻	0.195 ^c
SO ₄ ²⁻	0.300 ^c

^aMeasured and calculated in this work using Stokes' conductivity method.

^bObtained from Stokes et al.,^{S1} measured by their method.

^cObtained from reference,^{S3} determined by size exclusion column.

Table S3. Comparison among monovalent ion/divalent ion selectivity of various NFMs prepared by different methods.

Various membranes	Zeta potential (mV)	Monovalent/divalent ion pair	Monovalent ion rejection (%)	Divalent ion rejection (%)	Monovalent ion/divalent ion selectivity	Ref.
Polyelectrolyte layer-by-layer NFMs	~22	Na ⁺ /Mg ²⁺ ^a	-11 ± 2 ^a	95.0 ± 0.5 ^a	22.5 ± 2.3 ^a	[31]
Polyamide NFMs via interfacial polymerization	~-46	Cl ⁻ /SO ₄ ²⁻	40.8	95.4	12.9	[S4]
Homogeneous polysulfone NFMs	-60	Cl ⁻ /SO ₄ ²⁻	15	87	6.5	[S5]
Poly(N-vinylimidazole)gel-filled NFMs	~18	Na ⁺ /Mg ²⁺	80.3 ± 7.6	91.1 ± 3.2	2.9 ± 1.9	[14]
Cross-linked PEI NFMs	not given	Na ⁺ /Mg ²⁺	27.3	89.3	6.8	[S6]
Reduced graphene oxide NFMs	-43	Cl ⁻ /SO ₄ ²⁻	~42	~60	1.4	[S7]
PDA/PEI co-deposition NFMs after cross-linking	4.8 ± 0.6	Na ⁺ /Mg ²⁺	~47.9 ± 0.4	~95.6 ± 0.2	11.85 ± 0.65	[26]
MOF UiO-66 NFMs	not given	Na ⁺ /Mg ²⁺	47.0	98.0	26.5	[23]
PDA/PEI co-deposition NFMs	8.6 ± 0.50	Na ⁺ /Mg ²⁺	15.8 ± 0.5	88.5 ± 2.1	8.1 ± 0.9	this work
PDA/PEI co-deposition NFMs after reacting with MPSIs for 12 h	-9.5 ± 1.1	Cl ⁻ /SO ₄ ²⁻	16.0 ± 1.1	96.2 ± 0.6	22.7 ± 3.9	this work
			-15.2 ± 1.3 ^b	95.1 ± 0.3 ^b	23.6 ± 1.7 ^b	this work

^aNaCl/MgCl₂ mixed solution was used as the feed. ^bNaCl/Na₂SO₄ mixed solution was used as the feed.

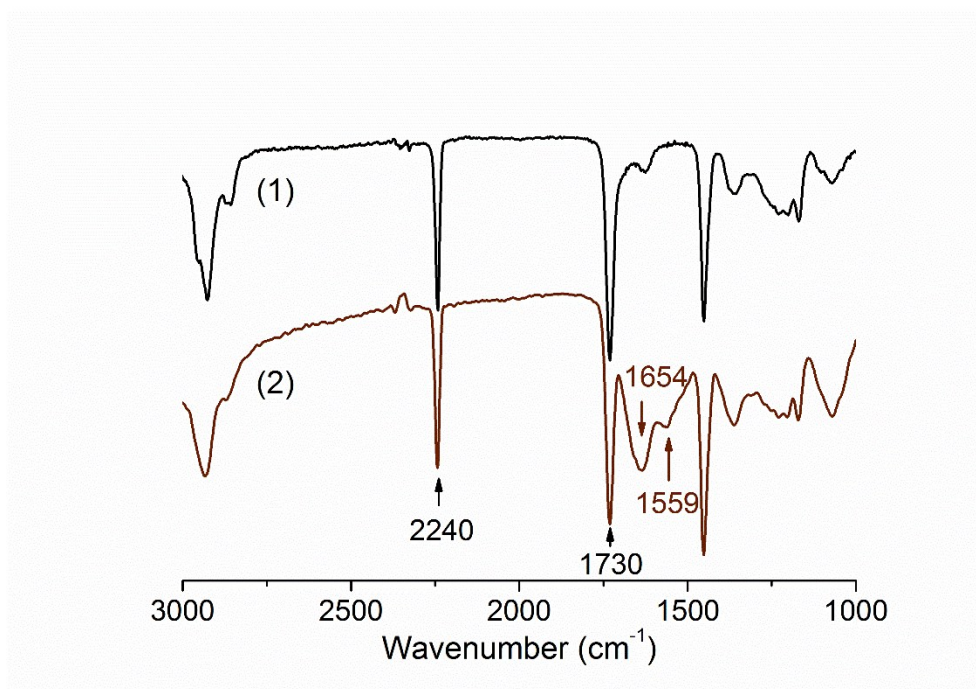


Fig. S1. FT-IR/ATR spectra of HPAN membranes (1) and PDA/PEI co-deposition NFMs (2).

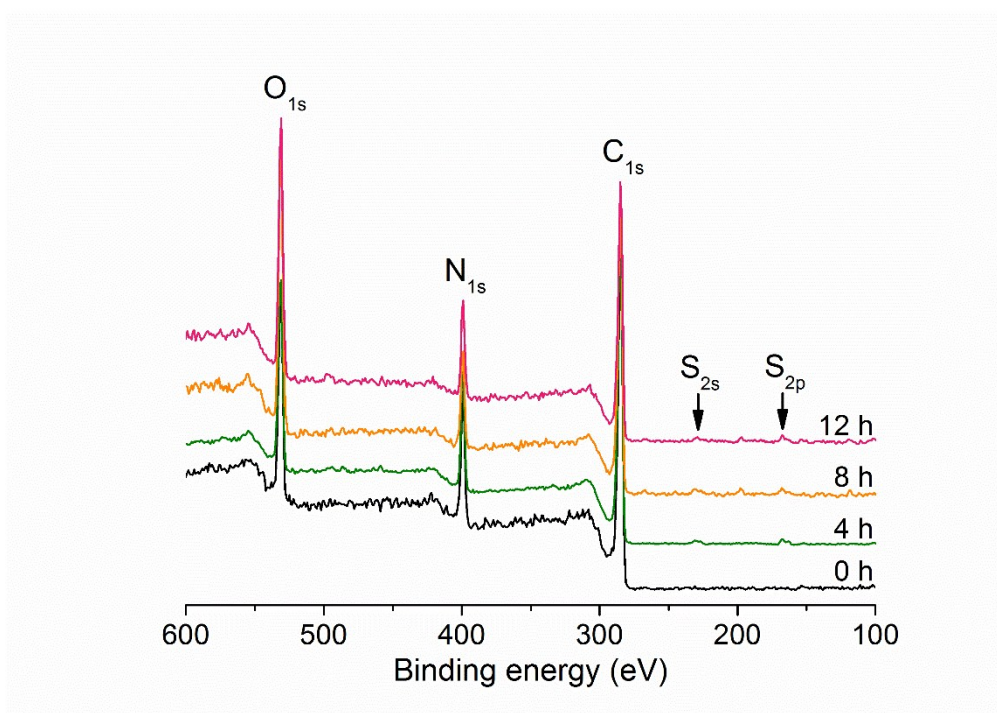


Fig. S2. XPS spectra of PDA/PEI co-deposition NFMs and the NFMs reacted with 2000 mg/L SMPS in a nanofiltration flat membrane module for different time. Operation conditions: T = 303 K, pH = 5.8, P = 0.6 MPa, cross-flow rate = 30 L/h.

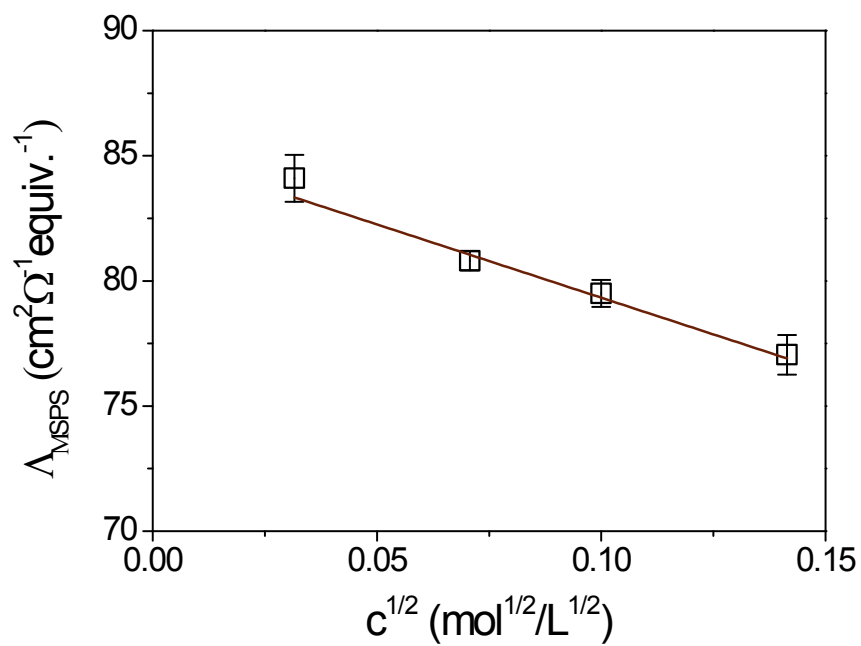


Fig. S3. Linear fitting of molar conductivity to the square root of sodium 3-mercapto-1-propanesulfonate (SMPS) concentration.

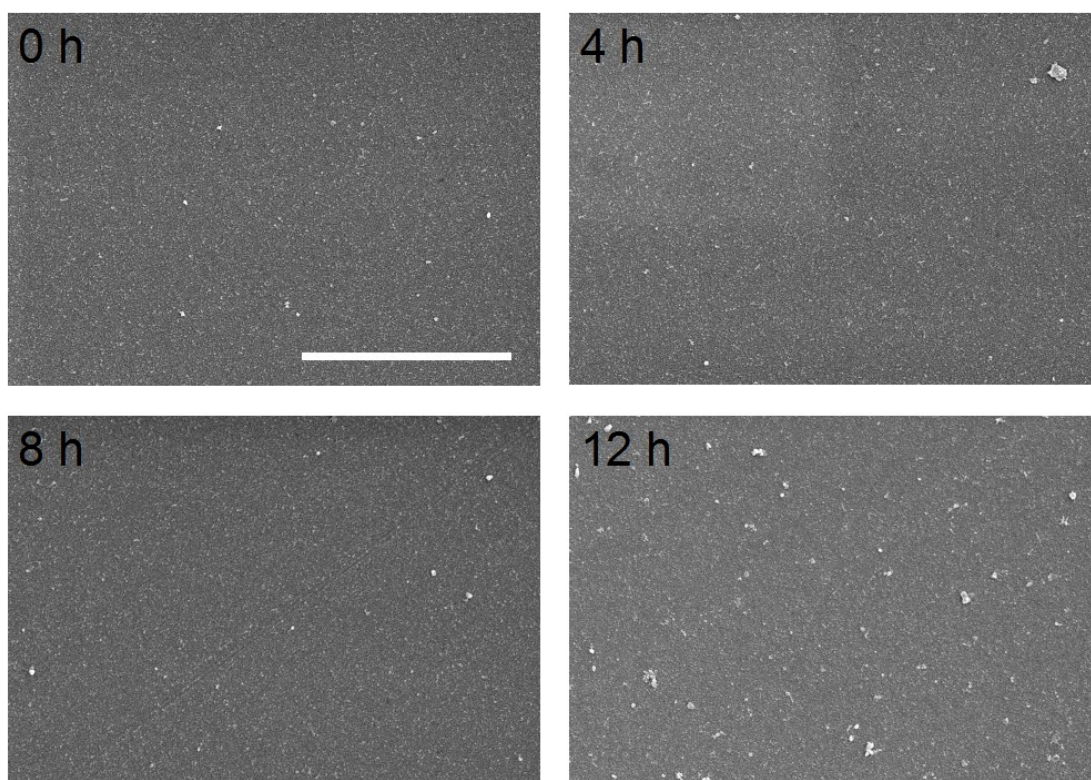


Fig. S4. Surface morphologies of various NFMs fabricated under the same condition as that in Fig. S2. Scale bar represents 5 μm .

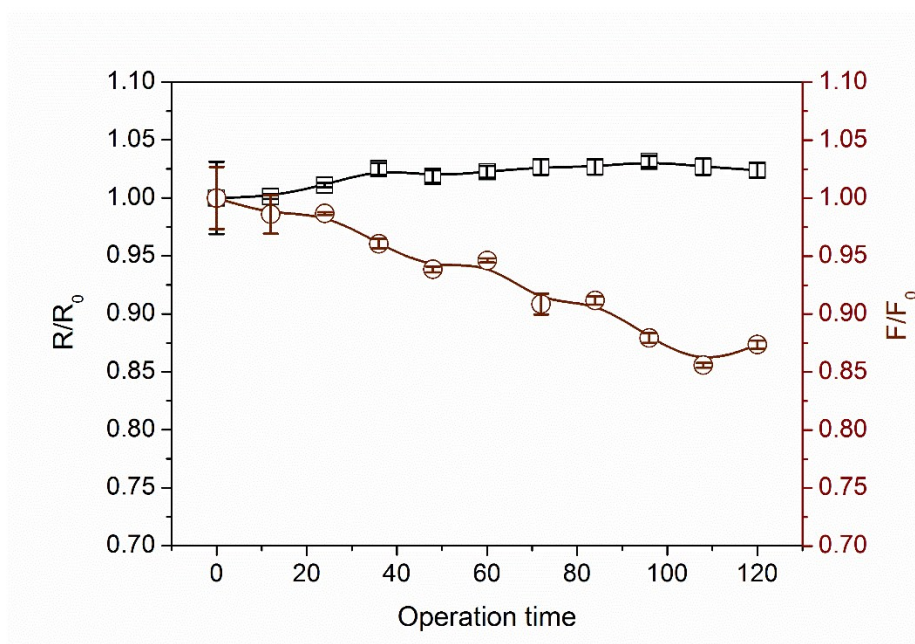


Fig. S5. Structure stability of the NFMs with different operation time. Operation conditions: Na_2SO_4 concentration = 2000mg/L, $T = 303$ K, $\text{pH} = 5.8$, $P = 0.6$ MPa, cross-flow rate = 30 L/h.

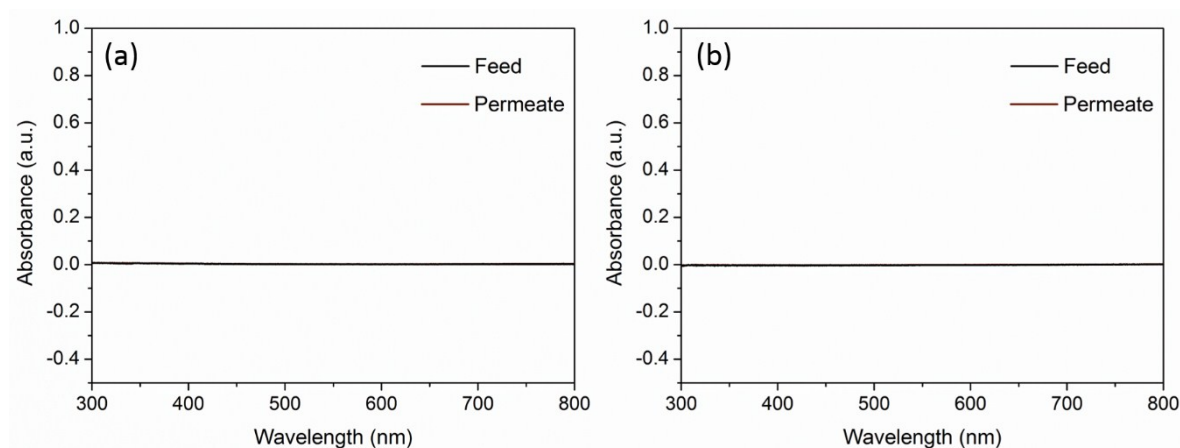


Fig. S6. UV-Vis spectra of (a) feed and permeate solutions after continuous operation for 120 h, (b) 0.1 mL feed or permeate solutions added in 0.2 mL DTNB solution and diluted to 3 mL after 15 min, with 0.1 mL ultra-pure water treated as the same being reference. The operation condition is the same as that in Fig. S5.

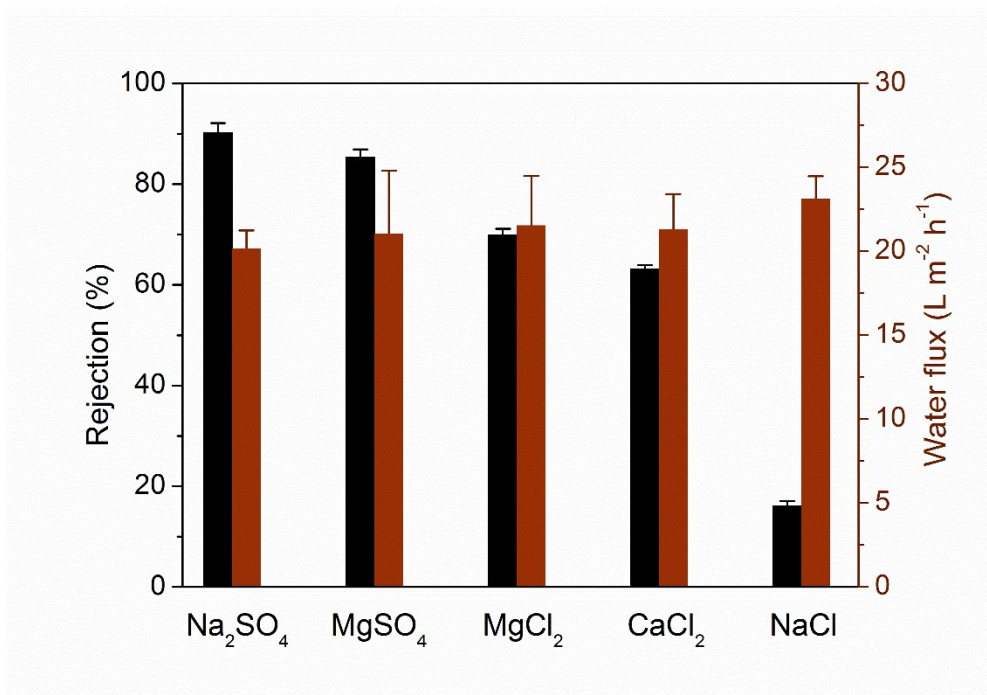


Fig. S7. Salt rejection and water flux of the NFMs fabricated by incubating PDA/PEI co-deposition membrane in 2000 mg/L SMPS at 30 °C for 24 h. Test conditions: inorganic salt concentration = 1000 mg/L, T = 303 K, pH = 5.8, P = 0.6 MPa, cross-flow rate = 30 L/h.

References

- [S1] R. A. Robinson and R. H. Stokes in *Electrolyte Solutions*, Butterworth & Co. (Publishers) Ltd., London, 1959, pp. 24-48.
- [S2] G. L. Ellman, *Arch. Biochem. Biophys.* 1958, **74**, 443.
- [S3] M. Y. Kiriukhin and K. D. Collins, *Biophys. Chem.*, 2002, **99**, 155.
- [S4] C. Zhou, Y. Shi, C. Sun, S. Yu, M. Liu and C. Gao, *J. Membr. Sci.*, 2014, **471**, 381.
- [S5] H.-G. Yuan, T.-Y. Liu, Y.-Y. Liu and X.-L. Wang, *Desalination*, 2016, **379**, 16.
- [S6] M. Li, J. Xu, C.-Y. Chang, C. Feng, L. Zhang, Y. Tang and C. Gao, *J. Membr. Sci.*, 2014, **459**, 62.
- [S7] Y. Han, Z. Xu and C. Gao, *Adv. Funct. Mater.*, 2013, **23**, 3693.