# Electronic Supplementary Material

## Ionic strength directed self-assembled polyelectrolyte single-bilayer membrane for low-pressure nanofiltration

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1. The separation performance of the substrate membrane Ms

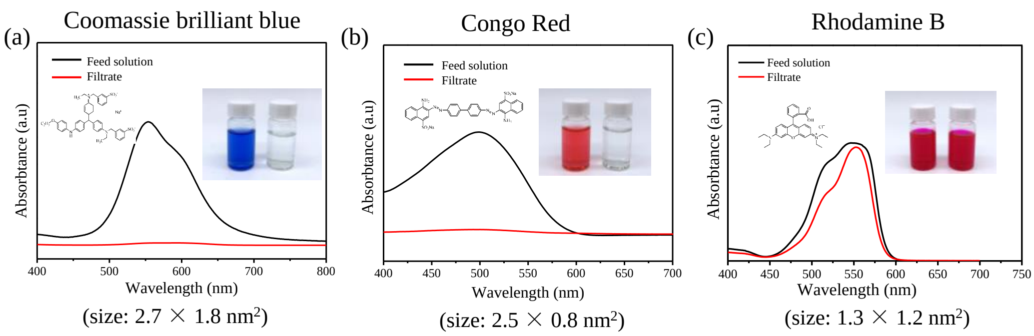


**Fig. S1**. The UV-spectra and the photographs of the dyes before and after filtrate through the Ms membrane

2. The cross-sectional SEM images of as-prepared PESB membranes

The cross-sectional SEM images of the single-bilayer membranes was shown in Fig. S2. It shows that with the increase of the background ionic strength, especially in the case of 1.0M, the layer of PEs becomes thicker. At low background ionic strength, it is hard to distinguish the edge between the substrate and the PE layer.

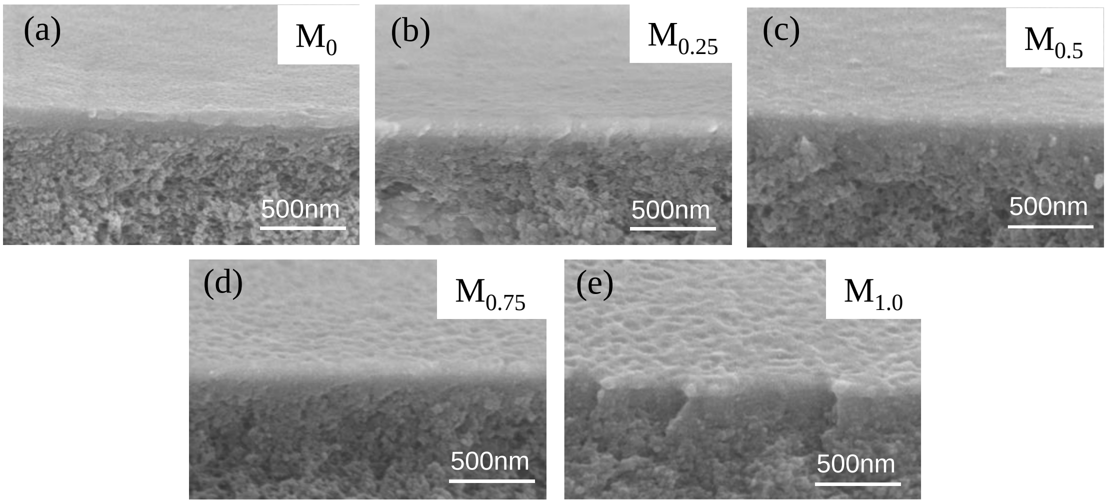


Fig. S2. Cross-sectional SEM images of as-prepared PESB membranes.

3. The AFM images and thickness measurement on the as-prepared PE membrane on silicon wafers.

To evaluate the effect of the background ionic strength on PE membrane thickness, we performed assembly experiment on smooth silicon wafers. Using a similar process as in Section 2.2 in the manuscript. Taken the background ionic strength of 0.25M and 1M as a typical example. The as-prepared samples were scratched with a sharp metal tweezer without damaging the silicon wafer. The dry-state thickness of was measured using a Bruker Dimension Fast Scan AFM equipment. We adjusted the cantilever tip to the edge of the scratch and captured a 4 μm× 4 μm AFM image at a scan rate of 1 Hz. We used the Section function in Nanoscope Analysis to determine membrane cross-sectional thickness by comparing scratched and non-scratched surfaces. As a result, the thickness of the PE bilayer on silicon wafer with salt concentration of 0.25M was approximately 33 nm, while the thickness of the PE bilayer with salt concentration of 1.0M was up to 76 nm which indicated the increment on thickness by increasing the background ionic strength.

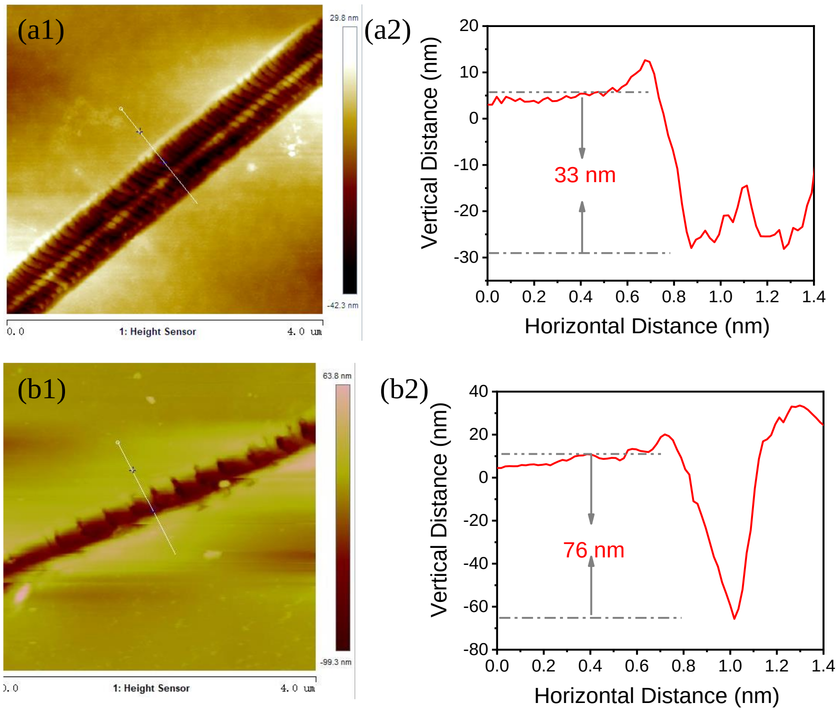


**Fig. S3**. AFM images and thickness measurement of the PE membranes on silicon wafers with background ionic strength of (a1-a2) 0.25 M and (b1-b2) 1.0 M.

3. Comparison of the separation performance of NF membranes prepared by the LBL method

Table S1 Comparison of the separation performance of NF membranes prepared by the LBL method

| Membranes | Dye | Salt | Rejection (%) | Permeance ($L/m^2hbar$) | Pressure (bar) | Ref |
|---|---|---|---|---|---|---|
| (PEI-ALG)/PSF-SPES | Congo red | — | 99.9 | 10 | 2 | [1] |
| (HPE-PDDA)/HPAN | Acid Fuchsin | — | 95.8 | 7.2 | 10 | [2 |
| (MOPM-$Fe^{3+}$)/PAN | Congo Red | — | 94.1 | 160.3 | 1 | [3] |
| $(ZIF\text{-}8\text{-}PSS)_{5.0}$/HPAN | Methyl Blue | — | 98.6 | 26.5 | 5 | [4] |
| (PEI-GA)/PAN | Congo Red | — | 97.1 | 25.5 | 2 | [5] |
| $(PDDA/GO)_{4.0}$/PAN | Congo Red | | 95.2 | 31.2 | 5 | [6] |
| | | NaCl | 18.9 | 7.48 | 5 | |
| $TpBD_{80}$/AAO | Evans Blue | — | 99.2 | 88.9 | 5 | [6] |
| VES/Agcl-PEI@HPAN | Crystal Cliolet | — | 99.2 | 106.4 | 1 | [8] |

| | | | | | | |
|---|---|---|---|---|---|---|
| | — | NaCl | 8.3 | 106.4 | 4 | |
| $TpBD_5$-HPAN | Congo Red | — | 98.6 | 339 | 1 | [9] |
| (pTNS-nTNS/PSF | — | NaCl | 96.5 | 0.5 | 15 | [10] |
| PEI-TA/$PGA_{pre}$ | — | $Na_2SO_4$ | 36.9 | 0.8 | 10 | [11] |
| | Methylene Blue | — | 36.9 | 86 | 10 | |
| $(PDDA\text{-}SPEEK)_{5.0}$/PAN | — | $Na_2SO_4$ | 64 | 14.21 | 6 | [12] |
| $(PSS\text{-}PAH)_{5.0}$/alumina | — | $MgCl_2$ | 95 | 7.37 | 4.8 | [13] |
| $(PDADMAC\text{-}PSS)_{4.0}$/NFG | — | $Na_2SO_4$ | 90 | 5.5 | 10 | [14] |
| ((PEI-modified GO)-PAA/PVA/GA)/PAN | — | NaCl | 37.8 | 12.4 | 5 | [15] |
| | Congo Red | — | 99.5 | 8.4 | 5 | |
| (ZIF-8-PEI)/HPAN | Congo Red | — | 99.2 | 76 | 1 | [16] |
| | — | $Na_2SO_4$ | 3.4 | 139 | 1 | |
| (PAA-PEI)/PDA-modified-membrane | — | $Na_2SO_4$ | 98.3 | 5.5 | 5 | [17] |
| (PDADMAC-PSS)/PAN | — | $Na_2SO_4$ | 97.1 | 14.2 | 1 | This work |

Supplementary References

1. Önder T, Sacide A A. Development of high flux nanofiltration membranes through single bilayer polyethyleneimine/alginate deposition. Journal of Colloid and Interface Science, 2019, 537: 215-227.
2. Joseph N, Thomas J, Ahmadiannamini P, Gorp H V, Bernstein R, Feyter S D, Smet M, Dehaen W, Hoogenboom R, Vankelecom I F J. Ultrathin Single Bilayer Separation Membranes Based on Hyperbranched Sulfonated Poly(aryleneoxindole). Advanced Functional Materials, 2017, 27(9): 1605068.
3. You X D, Wu H, Zhang R N, Su Y L, Cao L, Yu Q Q, Yuan J Q, Xiao K, He M R, Jiang Z Y. Metal-coordinated sub-10nm membranes for water purification. Nature Communications, 2019, 10: 4160.
4. Zhang R, Ji S L, Wang N X, Wang L, Zhang G J, Li J R. Coordination-Driven

In-Situ Self-Assembly Strategy for the Preparation of Metal–Organic Framework Hybrid Membranes. Angewandte Chemie, 2014, 53(37): 9775-9779.

5. Zhao S, Wang A. A loose nano-filtration membrane prepared by coating HPAN UF membrane with modified PEI for dye reuse and desalination. Journal of Membrane Science, 2017, 524: 214-224.
6. Wang L, Wang N X, Li J, Li J W, Bian W Q, Ji S L. Layer-by-layer self-assembly of polycation/GO nanofiltration membrane with enhanced stability and fouling resistance. Journal of Membrane Science, 2016, 160: 123-131.
7. Shi X S, Ma D W, Xu F, Zhang Z, Wang Y. Table-salt enabled interface-confined synthesis of covalent organic framework (COF) nanosheets. Chemical Science, 2020, 11: 989-996.
8. Shi X S, Wang R, Xiao A K, Jia T Z, Sun S P, Wang Y. Layer-by-Layer Synthesis of Covalent Organic Frameworks on Porous Substrates for Fast Molecular Separations. ACS Applied Nano Materials, 2018, 1, 6320-6326.
9. Liu S B, Wang Z, Ban M, Song P, Song X F, Khan B. Chelation-assisted in situ self-assembly route to prepare the loose PAN-based nanocomposite membrane for dye desalination. Journal of Membrane Science, 2018, 566, 168-180.
10. Ahmad N A, Goh P S, Wong K C, Zulhairun A K, Ismail A F. Enhancing desalination performance of thin film composite membrane through layer by layer assembly of oppositely charged titania nanosheet. Desalination, 2020, 476, 114167.
11. Cao Y, Zhang H R, Guo S W, Luo J Q, Wan Y H. A roust dually charged membrane prepared via catechol-amine chemistry for highly efficient dye/salt separation. Journal of Membrane Science, 2021, 629, 119287.
12. Ahmadiannamini P, Li X F, Goyens W, Meesschaert B, Vankelecom I F J. Multilayered PEC nanofiltration membranes based on SPEEK/PDDA for anion separation. Journal of Membrane Science, 2010, 360: 250-258.
13. Ouyang L, Malaisamy R, Bruening M L. Multilayer polyelectrolyte films as nanofiltration membranes for separating monovalent and divalent cations. Journal of Membrane Science, 2008, 310: 76-84.

14. Su B W, Wang T T, Wang Z W, Gao X L, Gao C J. Preparation and performance of dynamic layer-by-layer PDADMAC/PSS nanofiltration membrane. Journal of Membrane Science, 2012, 423–424: 324-331.
15. Wang N X, Ji S L, Zhang G J, Li J, Wang L. Self-assembly of graphene oxide and polyelectrolyte complex nanohybrid membranes for nanofiltration and pervaporation. Journal of Membrane Science, 2012, 213: 318-329.
16. Yang L B, Wang Z, Zhang J L. Highly permeable zeolite imidazolate framework composite membranes fabricated via a chelation-assisted interfacial reaction. Journal of Materials Chemistry A, 2017, 29(5): 15342-15355.
17. Chen Y L, Liu F, Wang Y, Lin H B, Han L. A tight nanofiltration membrane with multi-charged nanofilms for high rejection to concentrated salts. Journal of Membrane Science, 2017, 537, 407-415

4.The variations of PEG-1k rejection of the membrane after assembling PDADMAC with different NaCl concentration.

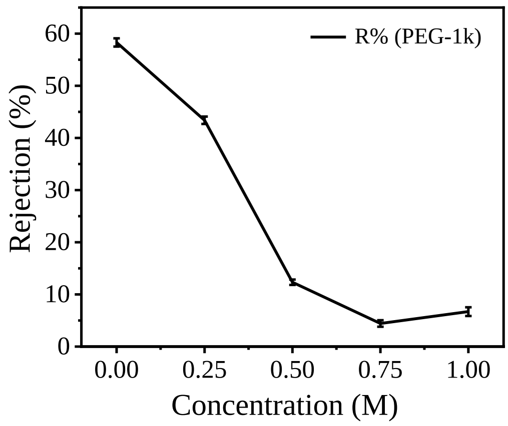


**Fig. S4**. The variations of PEG-1k rejection of the membrane after assembling PDADMAC with different NaCl concentration.

**5.** Separation performance of PESB membranes with different substrates.

**Table S2**. Separation performance of PESB membranes with different substrates.

| | Substrate properties | | | After assembly | |
|---|---|---|---|---|---|
| Samples | MWCO | WCA | Zeta Potential | PWF | REJ ($Na_2SO_4$) |

|  | (Da) | (°) | (mV) | (L m$^{-2}$ h$^{-1}$ bar$^{-1}$) | (%) |
|---|---|---|---|---|---|
| $M_s$ | 7300 | 0 | -9.8±0.2 | 19.7±2.3 | 97.1±1.8 |
| PES | 50000 | 57 | -7.8±0.5 | 309.2±5.4 | 3.5±1.8 |
| PAN | 50000 | 47 | -13.3±0.7 | 526.6±3.8 | 1.4±0.5 |

6. The SEM images of the PESB membranes with different substrates

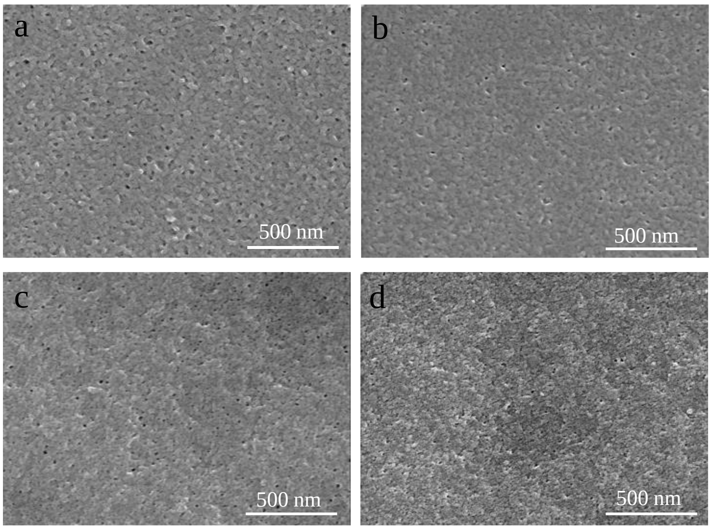


**Fig. S5.** The SEM images of PES, PES/(PDADMAC/PSS), PAN, PAN/(PDADMAC/PSS) membranes, respectively.