Nanofiltration membranes with narrow pore size distribution via contra-diffusion induced mussel-inspired chemistry

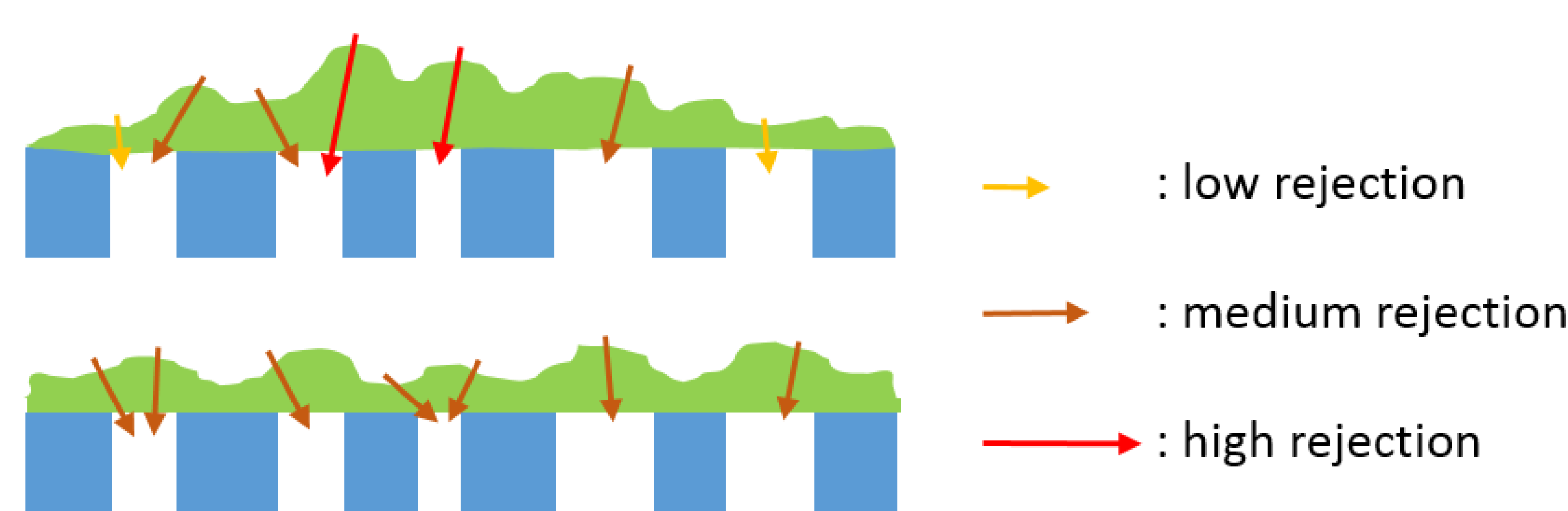Yong Du, Wen-Ze Qiu, Yan Lv, Zhi-Kang Xu*

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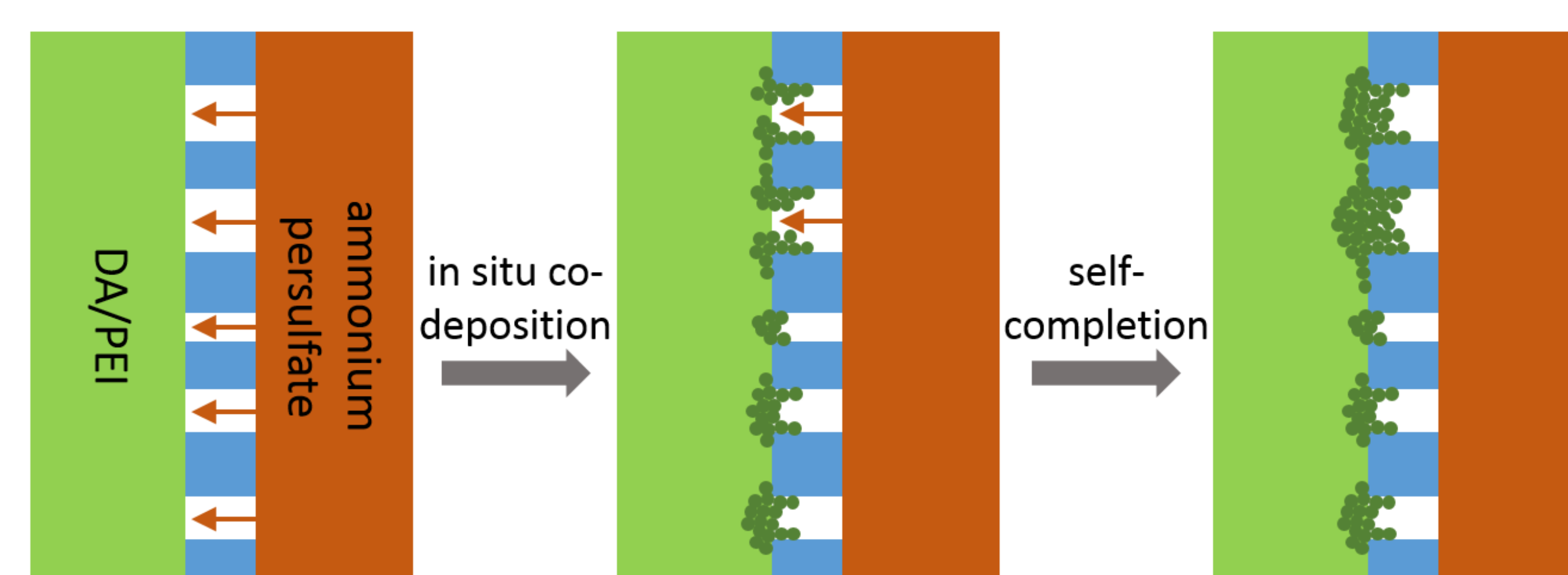
Introduction

Nanofiltration membranes (NFMs) have been widely used in desalination, waste water treatment and chemical product purification. Conventional NFM fabrication methods include phase inversion, interfacial polymerization, layer-by-layer assembly etc. However, thus prepared NFMs suffer from broad pore size distribution due to the non-uniform selective layer structure, which limits their applications, especially in complete separation of molecules with slight difference in molecular weights. Recently we have fabricated NFMs with fine-controlled structures via mussel-inspired chemistries such as the co-deposition of polydopamine (PDA) and polyethylenimine (PEI). Herein, defect-free composite NFMs with narrow size distribution are fabricated using a contra-diffusion method, with dopamine (DA)/PEI solution on the one side and $(NH_4)_2S_2O_8$ solution on the other side of the support ultrafiltration membrane. $S_2O_8^{2-}$ ions can diffuse towards the other side and in situ oxidize DA to form a co-deposition layer with PEI on the support. Larger pores in the support will be covered by a thicker layer of PDA/PEI since more $S_2O_8^{2-}$ ions will pass through these sites. Diffusion is hindered in those pores completely covered thus deposition is suppressed. The as prepared membranes have a highly uniform structure and narrow pore size distribution due to the self-completion effect. High selectivity on monovalent ions and divalent ions is achieved with such near electric neutral membranes ($MgCl_2$ rejection = 96%, NaCl rejection = 23%) majorly based on steric hindrance. Such membranes can be used in organic molecule separation such as isolating cellulose hydrogenation products.
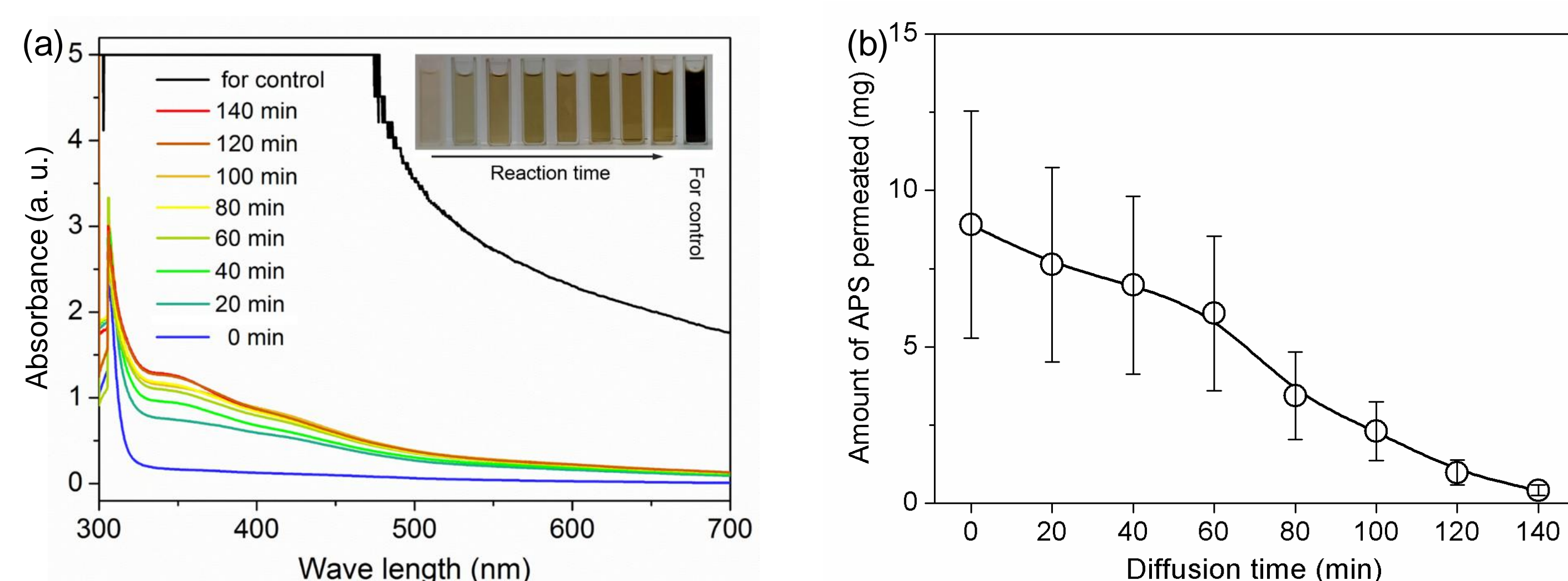
Results and Discussions

: low rejection

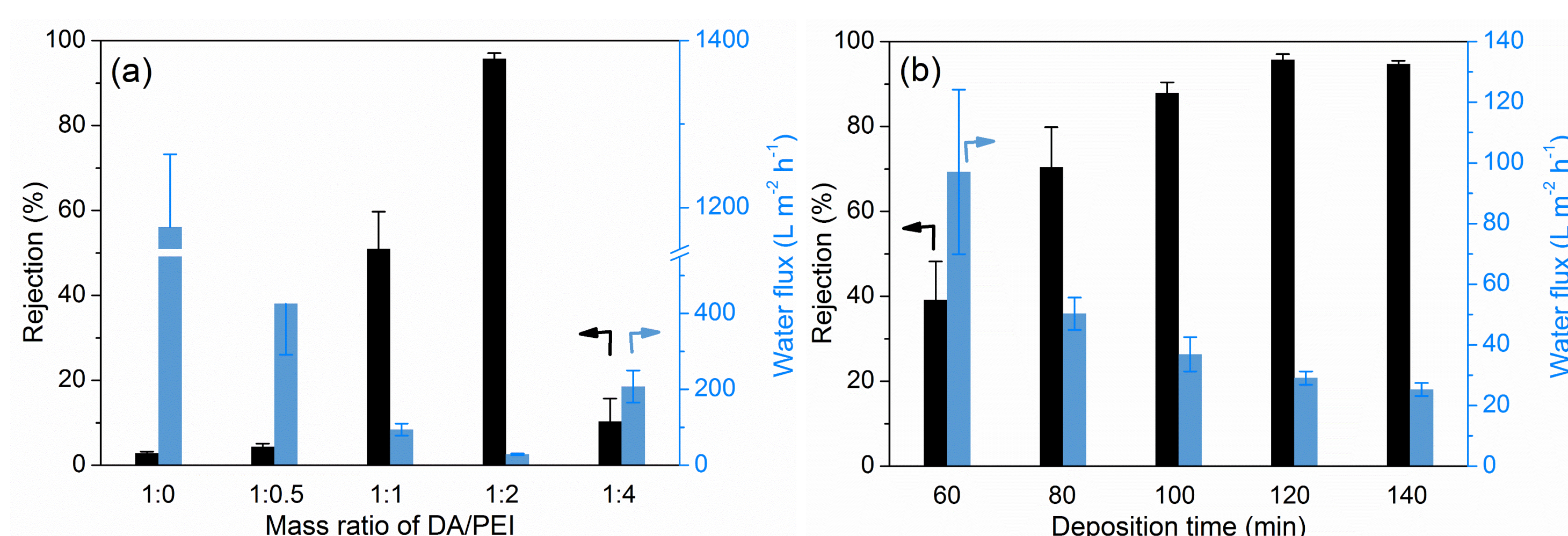**: medium rejection**

: high rejection

Scheme 1. Mass transport through NFM selective layers with non-uniform or uniform structures.
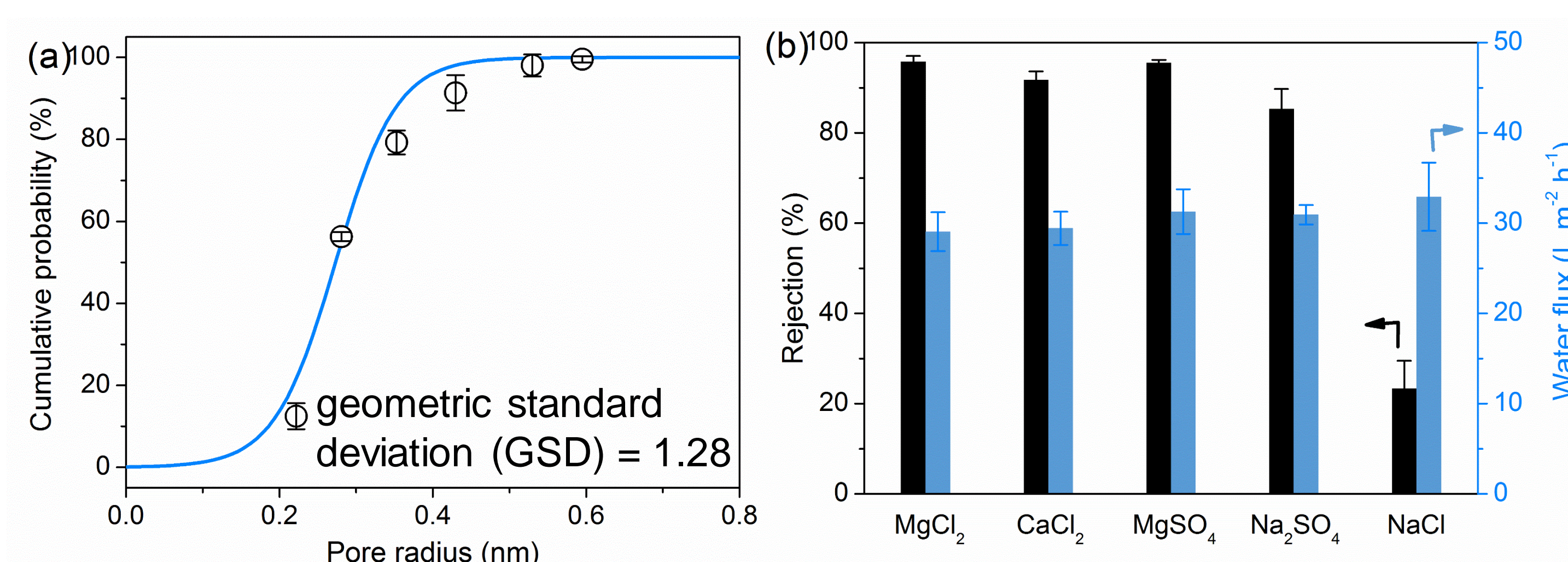

Scheme 2. illustration of the fabrication of the NFMs via contra-diffusion induced co-deposition.

Figure 1. (a) UV-vis spectra of DA/PEI solution after deposition for 0 to 140 min in a contra-diffusion device. Same amount of DA/PEI and $(NH_4)_2S_2O_8$ (APS) were added into one solution and was tested as control after incubated at 25 °C for 120 min. (b) Amount of APS that permeates through NFMs fabricated under the same condition (in 20 min in the same contra-diffusion device).
Only a small proportion of $S_2O_8^{2-}$ ions can permeate through the membrane and they are quickly reduced in the DA/PEI solution in such a contra-diffusion process. The diffusion of $S_2O_8^{2-}$ ions is significantly hindered by the formed PDA/PEI co-deposition layer.

Figure 2. Effects of DA/PEI ratio (a) and deposition time (b) on nanofiltration performance of the NFMs. Test conditions: $MgCl_2$ concentration = 1000 mg L^{-1}, pH = 5.8, T = 303 K, P = 0.6 MPa, cross-flow rate = 30 L h^{-1}.
The optimized fabrication condition is DA/PEI mass ratio = 1:2, deposition time = 120 min. More PEI is needed compared to the air induced co-deposition because the reaction rate of PEI with PDA needs to match with the DA oxidation rate. After deposition for 120 min, the $S_2O_8^{2-}$ ion diffusion is totally impeded.

Figure 3. Cumulative distribution of pore size (a) and nanofiltration performance (b) for different salts of the NFMs fabricated under the optimized condition (Test conditions: salt concentration = 1000 mg L^{-1}, pH = 5.8, T = 303 K, P = 0.6 MPa, cross-flow rate = 30 L h^{-1}.)
The as-prepared NFMs have ~90 nm uniform selective layers, with surface zeta potential ~2.5 mV. They have narrow pore size distribution, as measured by neutral solute rejection. The retention rate of various salts follows the order: $MgCl_2 \approx MgSO_4 > CaCl_2 > Na_2SO_4 >> NaCl$. The NFMs have high monovalent ion/divalent ion selectivity mainly based on size sieving effect. The Donnan exclusion only has minor influence on the rejection performance.

Table 1. Molecular separation performance of the NFMs fabricated under the optimized condition. Test conditions: salt concentration = 1000 mg L^{-1}, pH = 5.8, T = 303 K, P = 0.6 MPa, cross-flow rate = 30 L h^{-1}

Mixture	Larger molecule rejection	Smaller molecule rejection	Water flux (L m^{-2} h^{-1})
ethylene glycol/ glucose	89.3 ± 4.01%	11.2 ± 3.46%	30.5 ± 1.08
glycerol/ glucose	85.9 ± 3.96%	35.0 ± 3.39%	29.4 ± 1.78

The narrow pore size distribution is very useful in the separation of chemical products. For example, in cellulose hydrogenation, glucose (molecular weight (Mw) = 180) is the main product, with glycerol (Mw = 92) and ethylene glycol (Mw = 62) as byproducts. Mixtures of glycerol/glucose (molecular weight difference < 90) can be efficiently separated with the NFMs (rejection difference > 50%).

Conclusion

➢ NFMs are fabricated via contra-diffusion induced nature inspired chemistry.

➢ The as-prepared NFMs have uniform selective layer structures and narrow pore size distribution, which is useful in molecular separation.

➢ The NFMs have high selectivity on monovalent ion/divalent ion mainly due to size sieving effect.

Acknowledgment

Reference

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