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 (NH₄)₂SO₄ solution on the other side of the support ultrafiltration membrane. S₄O₆²⁻ ions 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 S₄O₆²⁻ 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 (MgCl₂ 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**

![Scheme 1. Mass transport through NFM selective layers with non-uniform or uniform structures.](image1)

![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 DAP and (NH₄)₂SO₄ (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 optimized condition (20 min) in the contra-diffusion device. Only a small proportion of S₄O₆²⁻ 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 S₄O₆²⁻ ions is significantly hindered by the formed PDA/PEI co-deposition layer.](image2)

![Figure 2. Effects of DA/PEI ratio (a) and deposition time (b) on nanofiltration performance of the NFMs. Test conditions: MgCl₂ 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 S₄O₆²⁻ ion diffusion is totally impeded.](image3)

![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 salutre rejection. The retention rate of various salts follows the order: MgCl₂ ≈ MgSO₄ > CaCl₂ > Na₂SO₄ > NaCl. The NFMs have high monovalent co/divalent ion selectivity mainly based on size sieving effect. The Donnan exclusion only has minor influence on the rejection performance.](image4)

**Table 1. Molecular separation performance of the NFMs fabricated under the optimized condition.**

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Larger anion rejection (%)</th>
<th>Smaller anion rejection (%)</th>
<th>Water flux (L m⁻² h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol/glucose</td>
<td>88.1 ± 3.20</td>
<td>11.2 ± 3.40</td>
<td>39.3 ± 1.08</td>
</tr>
<tr>
<td>Glucose/glucose</td>
<td>88.9 ± 3.90</td>
<td>33.0 ± 3.30</td>
<td>29.4 ± 1.78</td>
</tr>
</tbody>
</table>

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/ divalent ion mainly due to size sieving effect.

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**Reference**