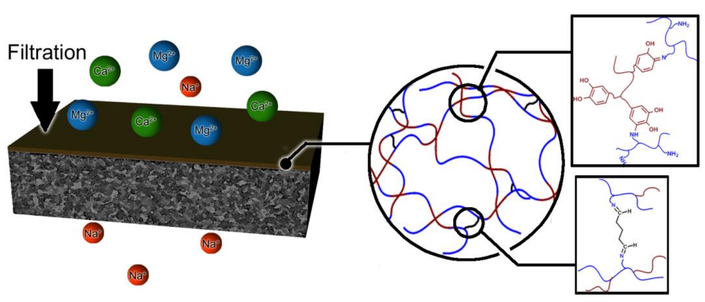
Nanofiltration Membranes via Co-deposition of Polydopamine/Polyethylenimine Followed by Cross-linking

Yan Lv (21329018), Hao-Cheng Yang, Hong-Qing Liang, Ling-Shu Wan, Zhi-Kang Xu*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China

Nanofiltration has become a rapidly developing and expanding area with tremendous potential for desalination, water softening and wastewater recycling due to its advantages of low operation pressure, high flux, high retention of multivalent ions and organic molecular (200-1000 Da). Nanofiltration membranes (NFMs) are mainly fabricated via the facile and fast interfacial polymerization technique. Nevertheless, the compatibility between the support layer and the skin layer is usually so poor that the skin layer can be easily detached from the substrate in harsh environments containing organic solvents such as ethanol. Mussul-inspired polydopamine can provide efficient interfacial binding ascribed to its great adhesive strength on various substrates. Beside, according to our previous work, the addition of low-molecular-weight PEI can reduce the self-aggregation of PDA to form particles and promote the homogeneous polymerization of dopamine. Herein, we fabricated a novel kind of composite NFMs with positively charged smooth surfaces via one-step co-deposition of PDA/PEI followed with crosslinking by glutaraldehyde (GA).



Graphical abstract

Fig.1 presents the fabrication process of the composite NFMs. PAN ultrafiltration membranes were hydrolyzed at first and then transferred into the fresh prepared dopamine/PEI solution and shaken at 25 °C for certain time after prewetted by ethanol. Afterwards, the PDA/PEI-modified membranes were immersed into GA ethanol solution for cross-link. Finally, the obtained NFMs were rinsed several times and used for filtration.

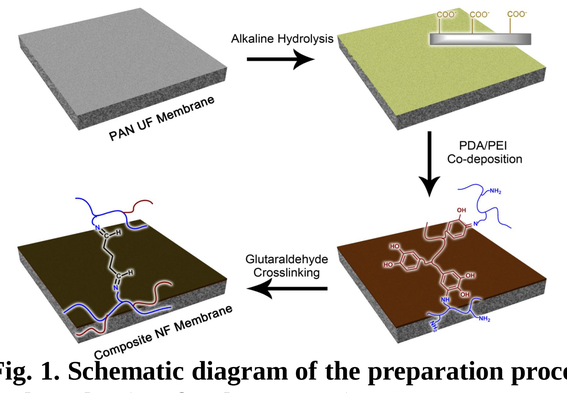


Fig. 1. Schematic diagram of the preparation process and mechanism for the composite NFMs.

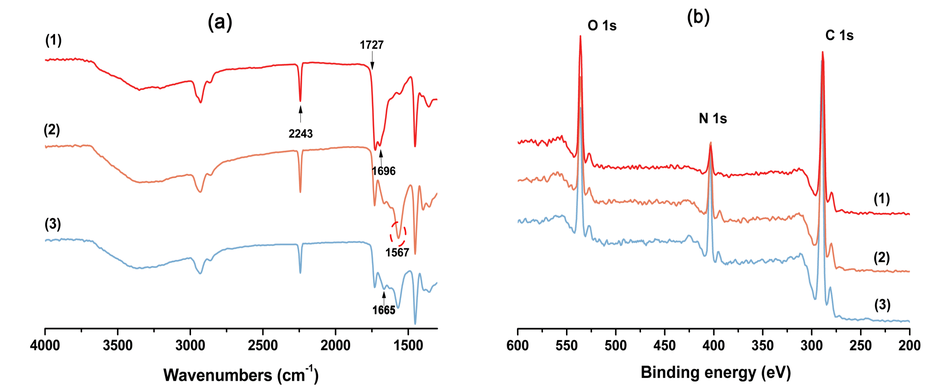


Fig. 2. FT-IR/ATR (a) and XPS (b) spectra of (1) the HPAN membrane, (2) the PDA/PEI-modified membrane (deposition time is 4 h), and (3) the composite NFM.

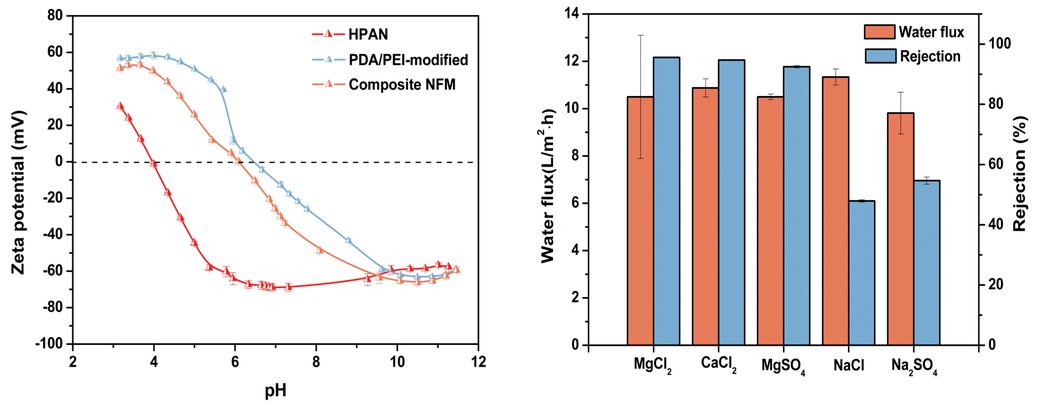


Fig. 5. Zeta potential of HPAN membrane, PDA/PEI-modified membrane and the composite NFM at various pH values and separation performance of the composite NFMs for different salts.

Table 1 Surface composition of the HPAN membrane, PDA/PEI-modified membrane (deposition time is 4 h) and composite NFM from XPS spectra (in atomic percent).

Samples	C 1s (%)	O 1s (%)	N 1s (%)
HPAN	70.66	13.90	15.44
PDA/PEI-modified	70.80	14.91	13.57
Composite NFM	72.59	19.67	7.43

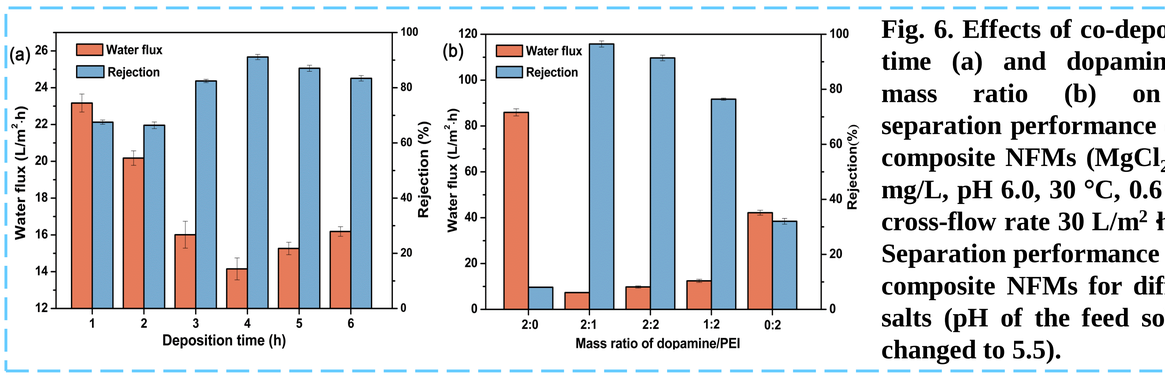


Fig. 6. Effects of co-deposition time (a) and dopamine/PEI mass ratio (b) on the separation performance of the composite NFMs ($MgCl_2$ 1000 mg/L, pH 6.0, 30 °C, 0.6 MPa, cross-flow rate 30 L/m² h) and Separation performance of the composite NFMs for different salts (pH of the feed solution changed to 5.5).

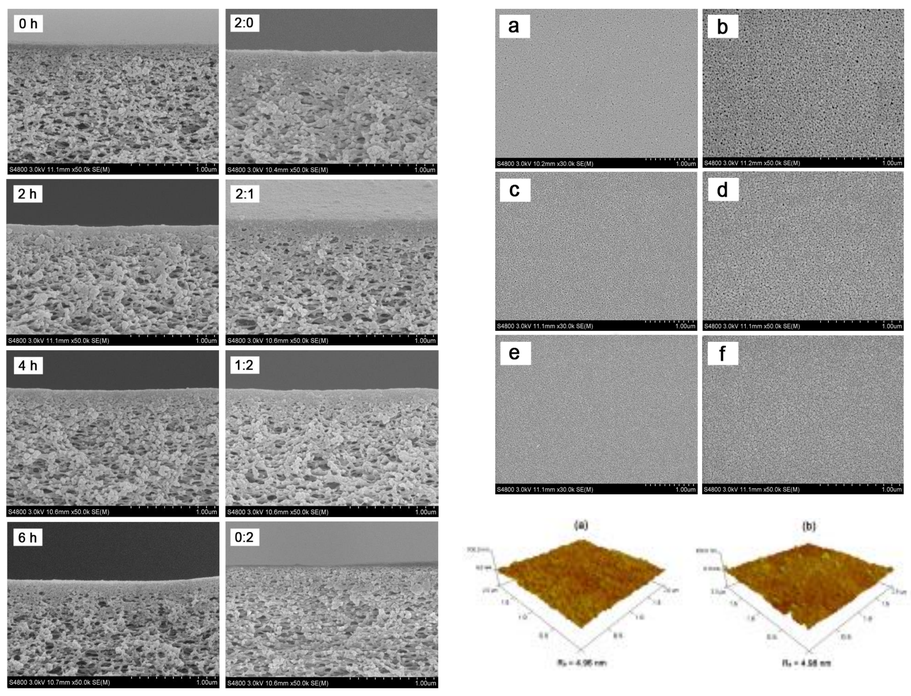


Fig. 3. Surface SEM images of (a,b) the HPAN membrane, (c,d) the PDA/PEI-modified membrane (deposition time is 4 h), and (e,f) the composite NFM. Cross-sectional SEM images of the composite NFMs with different co-deposition times and different dopamine/PEI mass. AFM images and mean surface roughness (R_a) of (a) the HPAN membrane and (b) the composite NFM

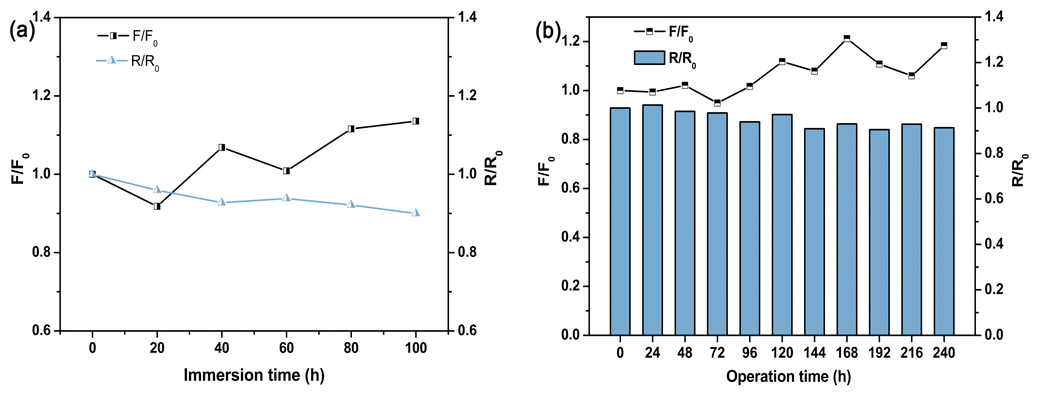


Fig. 7. The structural stability of the composite NFMs with different immersion time in ethanol (a) and different operation time (b). Test conditions: $MgCl_2$ concentration = 1000 mg/L, 30 ° C, pH = 6.0, 0.6 MPa, cross-flow rate = 30 L/m² h.

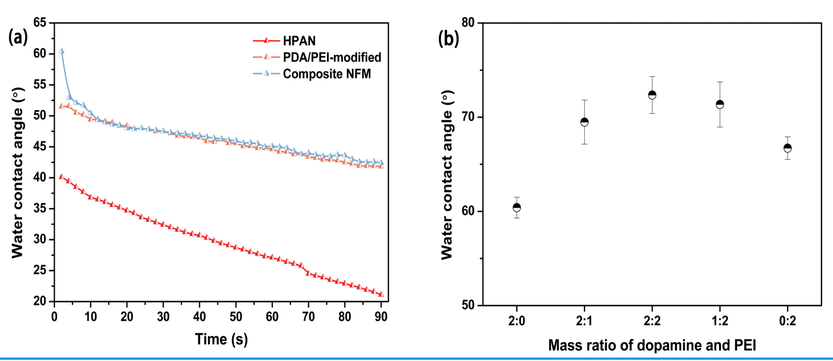


Fig. 4. Water contact angle of (a) different membranes, and (b) the composite NFMs with different dopamine/PEI mass ratios.

Conclusion:

A novel method was proposed to fabricate composite nanofiltration membranes by a facile co-deposition of PDA and PEI followed by glutaraldehyde cross-linking. The prepared membranes possess a uniform, smooth，robust and defect-free selective layer. The composite NFMs are slightly positively charged with high rejection performance (> 90%) for multivalent cations. Also, the composite NFMs exhibit excellent stability for ethanol and long-term operation.

References:

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