Supporting Information

Bio-inspired Ni²⁺-polyphenol Hydrophilic Network Achieving Unconventional High-flux Nanofiltration Membranes for Environmental Remediation

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Experimental Section

Materials

Lenzing P84 polyimide was purchased from HP Polymer GmbH. N-methyl-2-pyrrlione (NMP) was supplied by Tianjin Guangfu Fine Chemical Research Institute. Isopropanol (IPA), CuSO₄, FeCl₃•6H₂O, I₂, KI and BaCl₂ were obtained from Xilong Scientific Co., Ltd. 1,6-hexamethylenediamine (HDA), tannic acid (TA), AgNO₃, Co(NO₃)₂•6H₂O, Ni(NO₃)₂•6H₂O, Rose bengal (RB, MW = 1017.64) and Methyl blue (MB, MW = 799.80) were acquired from Aladdin Industrial Corporation (China). PEGs with molecular weight from 200 to 2000 Da were purchased from Sinopharm Chemical Reagent Co., Ltd. The water used during experiments was deionized water. All reagents were used without any further purification.

Preparation of ultrafiltration membrane support

Polyimide P84 ultrafiltration (UF) membranes were fabricated via phase inversion method. In order to minimize the systematic errors caused by personal factors and the change of the external environment during the process, cross-linked P84 UF membranes were used as the support layer¹. P84 was dried under 120 °C overnight to remove moisture before use. Dissolving 15 wt% of polyimide polymer in NMP to obtain the homogeneous dope solution, where the air bubbles were removed through keeping the solution at 65 °C for 12 h and then cooling to room temperature. The dope solutions were cast onto the glass using a casting knife with a fixed thickness of 200 µm. After allowing the solvent on membrane surface to evaporate about 10 s, the glass was then dipped in water parallelly. The membranes were precipitated from solution via phase inversion, which were subsequently placed in 2 wt% HDA in IPA for further crosslinking about 24 h. Then the membranes can be put in IPA and transferred to water before use.

Preparation of composite nanofiltration membranes

TA/Mⁿ⁺ (M represents Ag, Co, Ni, Cu, Fe) composite NF membranes were prepared by immersing

the P84 UF membranes into a fresh mixture of 10 mM of TA and 10mM of AgNO₃, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $CuSO_4$, $FeCl_3 \cdot 6H_2O$, respectively. All the membranes were deposited in the aqueous solution for 8 h to allow the networks complex formed on surface. At first, Ag⁺, Co^{2+} , Ni^{2+} , Cu^{2+} and Fe^{3+} were introduced as inorganic cross-linker in the coordination with TA. After separation test, we found that TA/Ni^{2+} coating endowed the composite NF membranes with better performance compared with others (Fig. 2). Hence, to discuss the influence of concentration on membrane structure and separation property further, the composite TA/Ni²⁺ coated NF membranes with ratio of 2:1, 1:1, 1:2 and 1:3 were fabricated.

Membrane characterization

Attenuated total reflection flourier transformed infrared spectroscopy (ATR-FTIR) measurements were performed using a Spectrum One instrument (Perkin Elmer, USA). All curves were determined in a range from 4000 to 500 cm⁻¹. XPS experiments were carried out on an AXIS ULTRADLD spectrometer (SHIMADZU, Japan) with Al K α X-ray source (1486.6 eV). And the survey scan spectra were recorded from 0 to 1100 eV. Membrane surface morphologies and composition were characterized by scanning electron microscopy (Hitachi S-4800) equipped with energy-dispersive spectroscopy (EDS). The membranes need to be broken in liquid nitrogen to observe the cross-sectional images. All the samples were sputtered with gold before SEM measurements. Atomic force microscopy (AFM) (Solver P47 AFM, Russia) was used to measure the roughness of the membranes in the tapping mode. The scan size to record the AFM image was kept 1 μ m×1 μ m. The water contact angles of membranes surface were characterized by a contact angle measuring system (G10 Kruss, Germany). The contact angle was taken at least five locations of the membrane and the average values were then calculated.

Separation performance of nanofiltration membranes

NF performance evaluation was carried out by a self-designed dead-end filtration device with a container volume of 250 mL (Fig. S1). The membrane sample with effective area of 21.2 cm² was sealed by a rubber O-ring. The trans-membrane pressure was adjusted to 0.5 MPa through linking to nitrogen tank. While testing, the pure water was allowed to permeate about 40 min to make the membranes stabilized. The feeding solution was maintained at magnetic stirring of 800 rmp to reduce the effect of concentration polarization. Permeation was calculated as given in Eq. (1).

$$Permeance = \frac{J}{\Delta P} = \frac{V}{At\Delta P}$$

(1)

Where J is the water flux through the membrane (L m⁻² h⁻¹), ΔP is applied pressure across the membrane (bar), V is the volume of permeated water (L), A is the effective area of membrane sample (m²) and t is the permeation time (h).

The rejection ratios of dyes were measured by RB and MB at the concentration of 50 ppm. After the pure water permeating through tested membrane for 40 min to obtain a steady state. The dye solution was poured into cell, and rejection was calculated using Eq. (2).

$$Rejection = \left(1 - \frac{Cp}{Cf}\right) \times 100\%$$
⁽²⁾

Where C_p and C_f are the concentrations of dyes in the permeated and feeding solutions (g/L), respectively. The dye concentrations were measured with a UV-Vis spectrophotometer (Hitach

UV-2800, Hitach Co., Japan). The maximum absorption wavelength of RB and MB are 558 nm and 607 nm, respectively.

Mean effective pore size and pore size distribution

Pore size distribution was determined as described elsewhere^[2]. Using u_p and σ_p , the pore size distribution of the nanofiltration membranes can be described as the following probability density function:

$$\frac{\mathrm{d}R(d_p)}{\mathrm{d}d_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp\left[-\frac{(\ln d_p - \ln u_p)^2}{2(\ln \sigma_p)^2}\right]$$
(3)

where dp is the pore diameter of the membrane. Ignoring the influences of the steric and hydrodynamic interactions between the solute and the pores on solute rejection, u_p (the mean effective pore radius) and σ_p (the geometric standard deviation) can be assumed to be the same as u_s and σ_g , and u_s is the geometric mean radius of the solute at R=50%, σ_g is the geometric standard deviation about u_s , which is defined as the ratio of the solute radius at R=84.13% and R=50%. PEG concentrations were determined by measuring absorbance at 535nm after iodine complexation with a UV–Vis spectrophotometer (Hitach UV-2800, Hitach Co., Japan)^[3,4].



Figure S1. Schematic illustration of the dead-end nanofiltration apparatus (1-nitrogen cylinder; 2-reguating valve; 3-pressure gauge; 4-solution container; 5-magnetic stick; 6-filtration membrane; 7-magnetic stirrer; 8-decompression valve; 9-beaker)



Figure S2. Survey scan spectrum of X-ray photoelectron spectra (XPS) of TA/Cu²⁺ coated composite nanofiltration membrane.

Table S1.

Elemental composition of P84 support, TA and TA/Fe³⁺ coated composite nanofiltration membrane.

	Composition (At. %)			
_	С	0	Ν	Fe
TA/Fe ³⁺ coated membrane	65.55	32.99	1.13	0.33
Tannic acid	60.7	39.3	/	/
P84 support membrane	72.38	16.88	10.74	/



Figure S3. AFM images of P84 ultrafiltration membrane and TA/metal ions coated composite nanofiltration membranes.

Table S2.

Surface roughness parameter (Ra) and water contact angle of P84 ultrafiltration membrane and composite nanofiltration membranes.

	Roughness(nm)	Contact angle (°)
P84 ultrafiltration support	1.84	61.2±1.04
TA/Ag ⁺ coated membrane	1.28	38.9±1.22
TA/Co ²⁺ coated membrane	1.69	31.9±0.78
TA/Ni ²⁺ coated membrane	1.53	27.5±1.43
TA/Cu ²⁺ coated membrane	1.15	33.4±1.89
TA/Fe ³⁺ coated membrane	1.03	44.8±0.92



Figure S4. Back side (A) and cross-sectional (B) SEM images of P84 support and TA/Ni²⁺ composite nanofiltration membranes with different ratios.



Figure S5. AFM images of coated composite nanofiltration membranes with TA/Ni²⁺ ratios of 2:1(a;b), 1:1(c;d), 1:2(e;f) and 1:3(g;h).



Figure S6. Probability density function curves of TA/Ni²⁺ coated membrane (TA/Ni²⁺=1:2).



Figure S7. Changes of dye removal and water flux with filtration time of the TA/Ni²⁺ coated membrane for filtration of 50 ppm dye aqueous solutions of methyl blue(TA/Ni²⁺=1:2).



Figure S8. Cross-sectional SEM images of coated composite nanofiltration membranes with TA/Ni²⁺ ratios of 2:1(left) and 1:5(right).



Figure S9. Separation performance of coated composite nanofiltration membranes with different TA/Co²⁺ ratios.

References

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