# Electronic Supplementary Information

# Three-channel capillary NF membrane with PAMAM-MWCNTs embedded inner polyamide skin layer for heavy metal removal

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**Contents: 14 Pages**

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## Materials and Methods

### Materials

PES (polyethersulfone, Mw = 58 kDa) was obtained from BASF company. N,N-dimethylacetamide (DMAc, AR) and diethylene glycol (DEG, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and used as solvent and non-solvent, respectively, for spinning solution. The substrates were prepared with non-solvent phase inversion method.

### Preparation of NF membranes

IP method was adopted to fabricate the NF membranes with inner skin-layer. PES substrate was firstly potted in a module and then fixed horizontally. The aqueous solution containing was circulated through the lumen side of the capillary by a rotary pump at 0.3 L/min for 2 min. Then, the residual droplets were removed by compressed air for 20 s across the membrane surface. TMC-hexane solution (0.15 wt% TMC) was then brought into contact with the amine saturated surface at a flow rate of 25.0 ml/min for 15 s. Therefore, a thin polyamide layer is formed on the inner surface of PES substrate as the selective layer. Finally, the prepared NF membranes were purged with clean air for 10 s to remove the residual hexane solution and were placed in an oven at 80 °C for 8 min. The fabricated NF membranes were stored in di-ionized water for later use.

### Preparation of the reaction products of MWCNTs and TMC

0.1% MWCNTs-PAMAM and MWCNTs-COOH aqueous solution were prepared respectively. 0.15% TMC n-hexane solution and the aqueous solution were mixed with equal volumes followed by shaking the mixture severely for 10 min. Then the mixture was filtrated and the residue was rinsed with plenty deionized water. Finally the residue was dried in an oven at 60℃ for 24 h followed by measured by XPS.

### Characterizations

The X-ray photoelectron spectroscopy (XPS, Thermo Fisher, UK) measurements were carried out to analyze the chemical composition of the original and modified MWCNTs and their reaction products with TMC.

### Membrane pore size distribution

Ethylene glycol, diethylene glycol, sucrose, PEG 400 and PEG 600 were used to measure the pore size and pore size distribution of the NF membranes. Feed solutions, 200 mg/L of these organic solutes, were separately flowed in the lumen side of the of the hollow fiber module under 4 bar. The permeate solutions from the shell side of the hollow fibers were collected after stabilization for 1 h. Both the feed and the permeate solutions were tested by a total carbon analyzer (Shimadzu, Model TOCVPN, Japan). The pore size distribution, the mean effective pore radius ($\mu_\mathrm{p}$) and the geometric standard deviation ($\sigma_\mathrm{p}$) of the membrane were therefore determined by the correlation between rejection and radius of the four solutes as described elsewhere.[1,2] The MWCO is defined as the molecular weight of a solute, 90% of which is retained by the membrane. $\mu_\mathrm{p}$ is equal to the radius of the solute at $R$=50%, and $\sigma_\mathrm{p}$ is the ratio of the solute radius when $R$=84.13% over the solute radius when $R$=50%. Then the pore size distribution of the membrane can be expressed as follows:

$$\frac{dR(r_\mathrm{p})}{dr_\mathrm{p}} = \frac{1}{r_\mathrm{p} \ln \sigma_p \sqrt{2\pi}} \exp\left[ -\frac{(\ln r_\mathrm{p} - \ln \mu_\mathrm{p})^2}{2(\ln \sigma_p)^2} \right]$$

## Adsorption measurements

In order to test the adsorption capacity of the NF membranes, three fibers with an effective length of 3.0 cm per fiber for each NF membrane were immersed in 30 ml 50 mg/L $Pb^{2+}$ aqueous solution with a pH of 6.0 shaken at 60 rpm continuously for 48 hours. The adsorption capacity of the substrate was also tested in the same way for a control experiment. The adsorption capacity of different membranes was calculated through the equation, $m = V(c_0 - c_1)/A$, where $m$ is the adsorption capacity (mg/m$^{-2}$), $V$ is the volume of the ciprofloxacin solution (mL), $A$ is the membrane surface area (cm$^2$), $c_0$ is the original concentration and $c_1$ is the concentration (mg/L) after 48 hours.

## Dispersion of MWCNTs

The MWCNTs-COOH and MWCNTs-PAMAM are stable in 1.0% PIP aqueous solution as shown in Fig. S1. While MWCNTs-COOH are more stable than MWCNTs-PAMAM, and this phenomenon may lie in two reasons. One is that PAMAM with the size of 4.4 nm increases the size of MWCNTs and astricts the dispersion of MWCNTs in aqueous solution. The other is that the unreacted –COOH may hydrolyze in aqueous solution forming –COO$^-$, and these negative groups –COO$^-$ can interact with abundant –NH$_2$ in PAMAM, accelerating the reunion and sedimentation of MWCNTs.

## Grafting degree of PAMAM on MWCNTs-COOH

The grafting degree of PAMAM on MWCNTs-COOH was calculated from the TG results. The –COOH content is actually 3.86% on MWCNTs-COOH, and it is 4.2% from TG results which approximates the exact content of –COOH. Thus, the grafting degree (9.85%) of PAMAM on MWCNTs-COOH can be calculated based on the weight loss (13.7%) of MWCNTs-PAMAM from 100-600 ℃ and the reaction between MWCNTs-COOH and PAMAM.

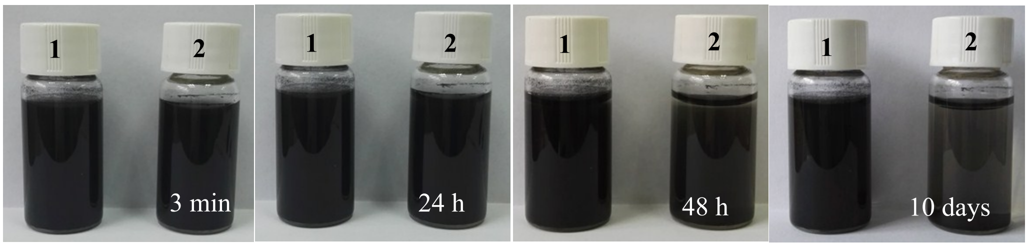

Fig. S1. The stability of MWCNTs-COOH (1) and MWCNTs-PAMAM (2) in 1.0% PIP aqueous solution (The concentrations of both MWCNTs-COOH and MWCNTs-PAMAM are 0.1%).

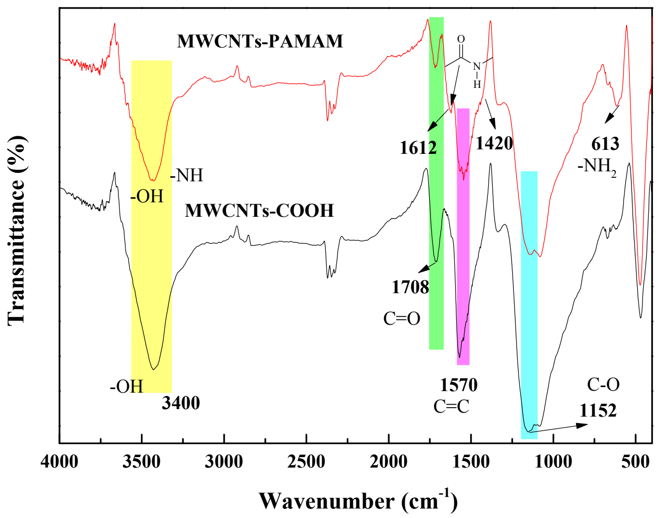

Fig. S2. FTIR spectra of original and modified MWCNTs.

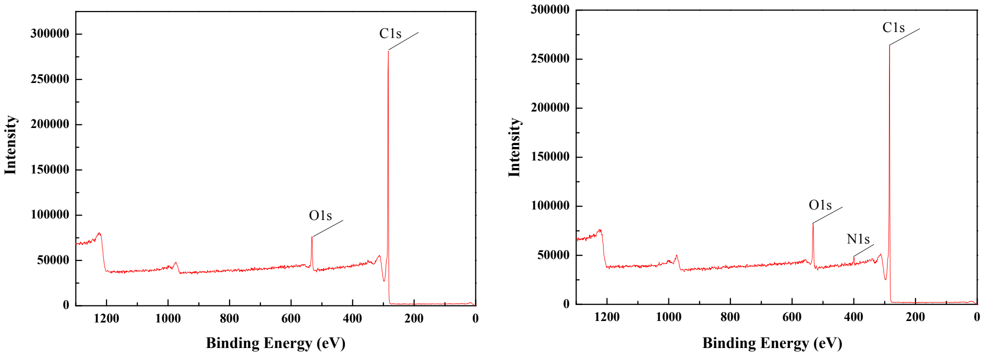

Fig. S3. XPS spectra of the products of MWCNTs-COOH and MWCNTs-PAMAM between TMC.

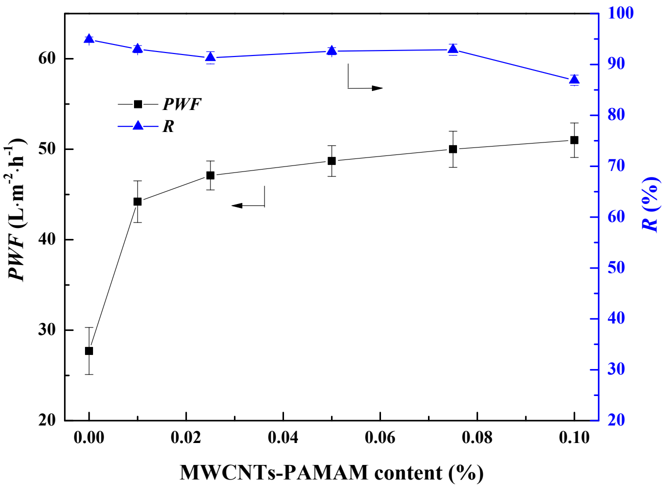

Fig. S4. Effect of MWCNTs-PAMAM on the permeation and separation performance of NF membranes. (NF membranes were prepared with PIP 1.0%, TMC 0.15%, aqueous solution immersion time 3 min, reaction time 15 s and heat treat at 80 °C for 8 min.)

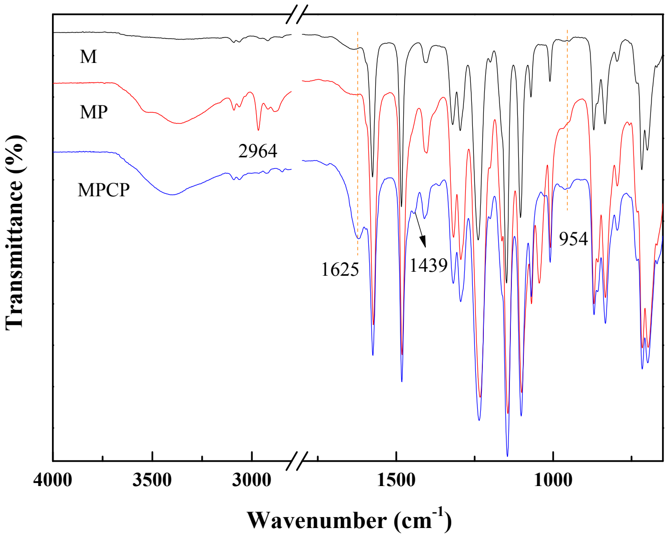

Fig. S5. FTIR spectra of substrate and NF membranes.

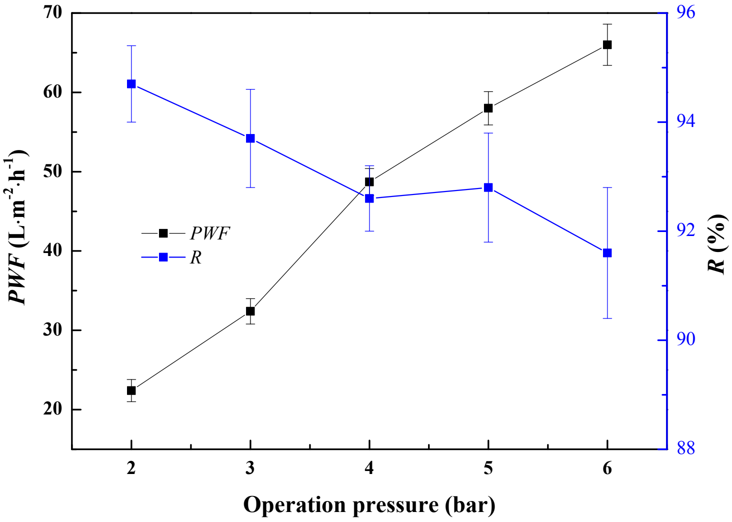

Fig. S6. The permeability and rejection performance of MPCP membrane under different operation pressure.

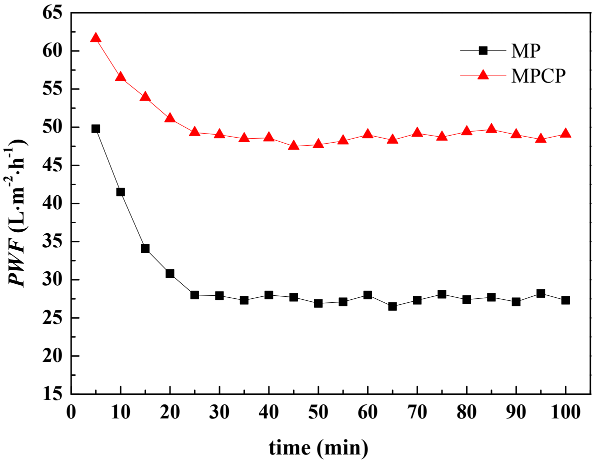

Fig. S7. Pure water flux of MP and MPCP membranes versus time.

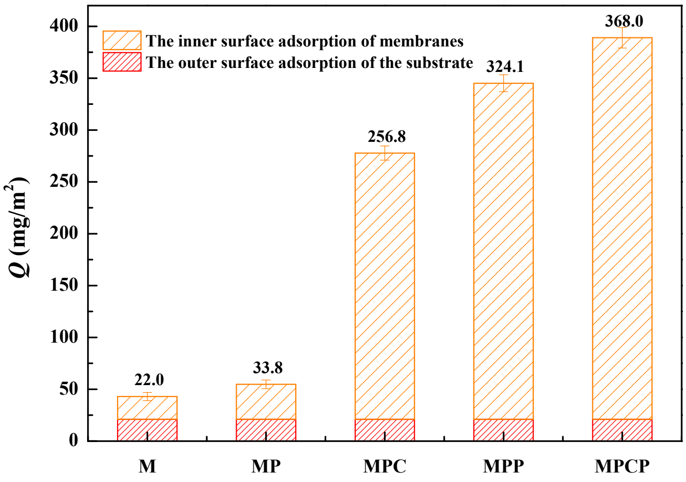

Fig. S8. The adsorption capacity of NF membranes for $Pb^{2+}$. Each membrane sample with the length of 3.0 cm was immersed into 10 mL 50 mg/L $Pb^{2+}$ aqueous solution for 24 h, and the pH of the solution was 5.0.

Table S1 The composition of MWCNTs-COOH and MWCNTs-PAMAM after reaction with TMC.

| Samples | Atom percent (at%) | | | C/O | N/O |
|---|---|---|---|---|---|
| | C 1s | O 1s | N 1s | | |
| MWCNTs-COOH before reaction with TMC | 94.40 | 5.60 | 0 | 16.86 | / |
| MWCNTs-COOH after reaction with TMC | 93.41 | 6.59 | 0 | 14.17 | / |
| MWCNTs-PAMAM before reaction with TMC | 86.32 | 8.11 | 5.57 | 10.64 | 0.69 |
| MWCNTs-PAMAM after reaction with TMC | 89.96 | 8.12 | 1.92 | 11.08 | 0.24 |

## References

[1] J. Gao, S.-P. Sun, W.-P. Zhu,T.-S. Chung, Polyethyleneimine (PEI) cross-linked P84 nanofiltration (NF) hollow fiber membranes for $Pb^{2+}$ removal, J. Membr. Sci. **452** (2014) 300-310.

[2] W.-P. Zhu, J. Gao, S.-P. Sun, S. Zhang,T.-S. Chung, Poly(amidoamine) dendrimer (PAMAM) grafted on thin film composite (TFC) nanofiltration (NF) hollow fiber membranes for heavy metal removal, J. Membr. Sci. **487** (2015) 117-126.