Supporting information for

Ultrathin Nanofiltration Membrane from Confined Polymerization within Nanowires Network for High-Efficient Divalent Cations Removal

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Experimental section

***Materials*:** Trimesoyl choride, branched polyethylenimine (PEI, Mw=600, 1800, 10,000 and 70,000 Da) and Tris(hydroxymethyl)aminomethane were purchased from Aladdin Co., Ltd. (Shanghai, China). SWCNTs (diameter < 2 nm, length: 5-50 μm, purity: > 95%) were obtained from XFNANO (Nanjing, China). Sodium dodecylbenzenesulfonate and D-Raffinose pentahydrate was purchased from J&K Scientific Ltd. Dopamine hydrochloride was purchased from Alfa-Aesar. Epoxy-Embedding Kit 45359 was purchased from Sigma-Aldrich. PES MF membranes (pore size: 0.45 μm) were provided by Yibo Co., Ltd. (Haining, Zhejiang province, China). Other chemicals were all obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China).

***Preparation of SWCNT network film*:** 20 mg SWCNT was added into 200 ml sodium dodecylbenzenesulfonate aqueous solution (2 mg ml^{-1}) and sonicated at power of 300 W for 36 h. The obtained SWCNT dispersion was centrifuged (10,000 rpm, 30 min), after which 150 ml supernatant was collected and diluted 3 times by pure water. 45 mg polydopamine (PD) was added into the diluted dispersion (450 ml) and stirring at 40°C for 1 h. 45 ml Tris buffer (0.1 M, pH 8.5) was then added into it and the reaction was kept at 40°C for 48 h. The obtained brown dispersion (PD-wrapped SWCNT) was centrifuged (10,000 rpm, 30 min) and again the supernatant was collected, stored at 4°C for further use. SWCNT film was prepared by vacuum filtration method. Specifically, a certain amount of the PD-wrapped SWCNT dispersion (26.5 μg ml^{-1}) was diluted with ethanol and vacuum-filtrated (vacuum pressure of 0.02 MPa) onto PES MF membrane. Area of the SWCNT film is 11.6 cm^2, which is dependent on the size of the filter. For SWCNT dispersion volume of 0.25 ml, 0.5 ml and 1 ml, the resultant density of SWCNTs on PES MF membranes are 0.58 μg cm^{-2}, 1.1 μg cm^{-2} and 2.3 μg cm^{-2}, respectively. The obtained SWCNT film was dried in air before use.

***Deposition of PEI and in situ crosslinking reaction*:** The as-prepared 11.6-cm^2 SWCNT film was immersed in the PEI aqueous solution (5 mg ml^{-1}) for 1 min. After taken out, the film was attached to a hydrophilic glass plate to draw the excess solution from back side of the membrane, dried in the air until no water spot was remained on the surface. Then 2 ml TMC hexane solution of 0.6 mg ml^{-1} was dropped onto the surface of SWCNT film (edge sealed by a filtration cup). After reacting for 1 min, excess TMC solution was removed and the film was washed by hexane and then cured in oven at 60°C for 25 min. The obtained membrane was washed with pure water for several times and preserved in water for use. To obtain the free-standing PA/SWCNT active layer, the NF membrane was immersed into *N,N*-dimethylformamide to dissolve the underlying PES, and the solvent was refreshed every 6 hours for 4 times.

***Nanofiltration performance test*:** Nanofiltration performance of the membranes was tested in a cross-flow filtration apparatus with effective area of 7.1 cm^2. Applied pressure was maintained at 5 bar and the flow rate was 45 L h^{-1}. The concentration of feed solution was 1000 ppm for all salts (unless otherwise noted) and 200 ppm for neutral molecules (glycerol, glucose, sucrose and raffinose), and the temperature was kept at 28°C. Membrane filtration was conducted at least 1 h before all measurements were taken. Rejections for salts were determined by conductivity (detected by a Mettler Toledo FE30K) of the feed and filtrate solutions. Rejection for neutral molecules was calculated by total organic carbon content of the feed and filtrate solutions.

***Characterization*:** SEM images were obtained from a Hitachi S4800 cold field emission scanning electron microscope. The cross-sectional TEM image was taken from a FEI Tecnai G2 F20 S-TWIN transmission electron microscopy. Specifically, a small piece of membrane was fixed using embedding resin and then cut by a Leica EM UC7 ultra-microtome, and the obtained sample slice was used for TEM observation. AFM images were taken from a Bruker's Dimension Icon atomic force microscopy. XPS was measured by a Thermo Fisher

Scientific Escalab 250Xi equipped with Al Kα X-Ray source. Surface zeta potential was tested by an Anton Paar SurPass electrokinetic analyzer using electrolyte of 1 mM KCl. Contact angles were measured on a Data-Physics OCA 20 with 3 μl water droplet. Total organic carbon (TOC) was measured by OI Analytical Aurora Model 1030.

Supplementary Figures

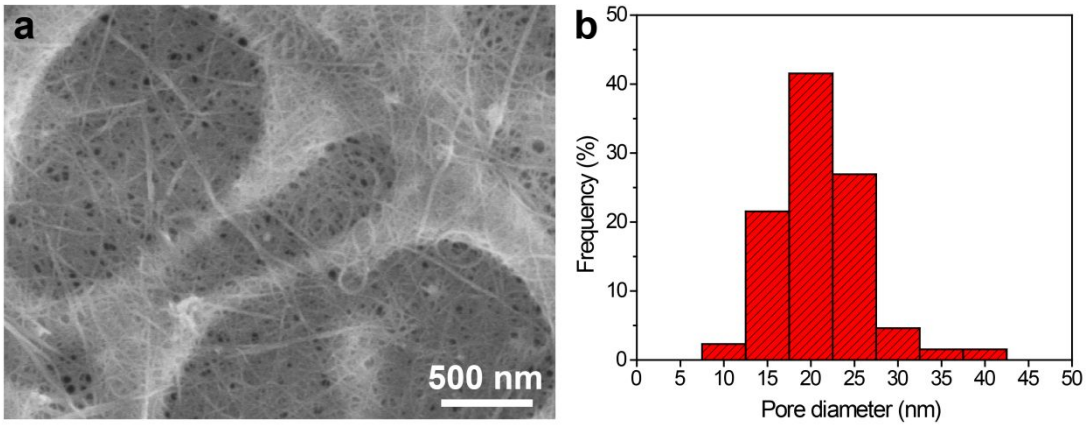

Figure S1. (a) SEM image of the pristine SWCNT network film with SWCNT density of 2.3 μg cm^{-2} and (b) its pore size distribution.

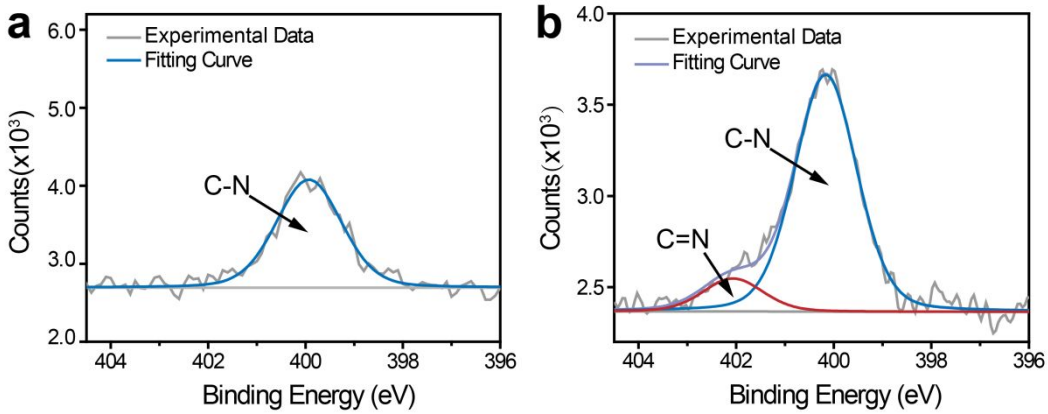

Figure S2. N1s XPS spectra of (a) pristine SWCNT network film and (b) PEI deposited SWCNT film with water washing. After depositing PEI for 1 min, this film was immediately washed with water instead of the crosslinking procedure.

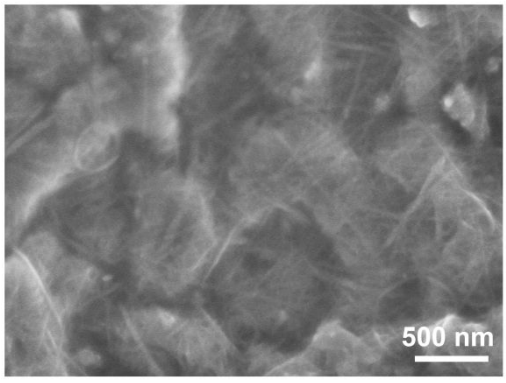

Figure S3. SEM images of the SWCNT network where the deposited PEI 600 was crosslinked by TMC without water washing.

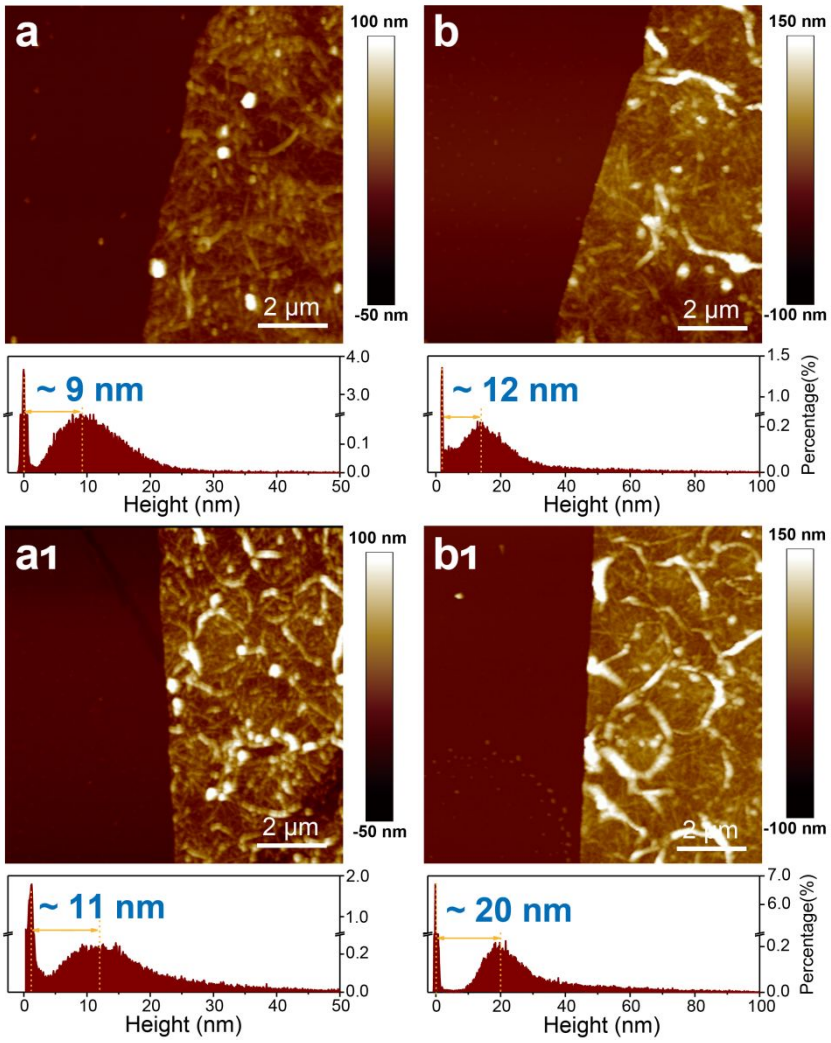

Figure S4. AFM images and corresponding statistical height distributions of pristine SWCNT film with SWCNT density of (a) 0.58 μg cm^{-2} and (b) 1.1 μg cm^{-2}, and correponding PA/SWCNT active layers prepared with PEI 600 (a1, b1). **Note:** Thickness of the SWCNT network can be tuned by adjusting the SWCNT depositing volume. In addition to the 31-nm SWCNT network film (with deposition volume of 1 ml, 26.5 μg ml^{-1}), these two SWCNT network films with SWCNT deposition volume of 0.25 ml and 0.5 ml were prepared to give thicknesses of 9 nm and 12 nm. The corresponding thicknesses of the PA/SWCNT active layers (prepare with 5 mg ml^{-1} PEI 600 and 0.6 mg ml^{-1} TMC) are 11 nm and 20 nm, respectively. This result shows that the generation of PA layer has little impact on the thickness of pristine SWCNT network. It indicates that PA layers localize inside the networks and form interpenetrated structures regardless of the film thickness.

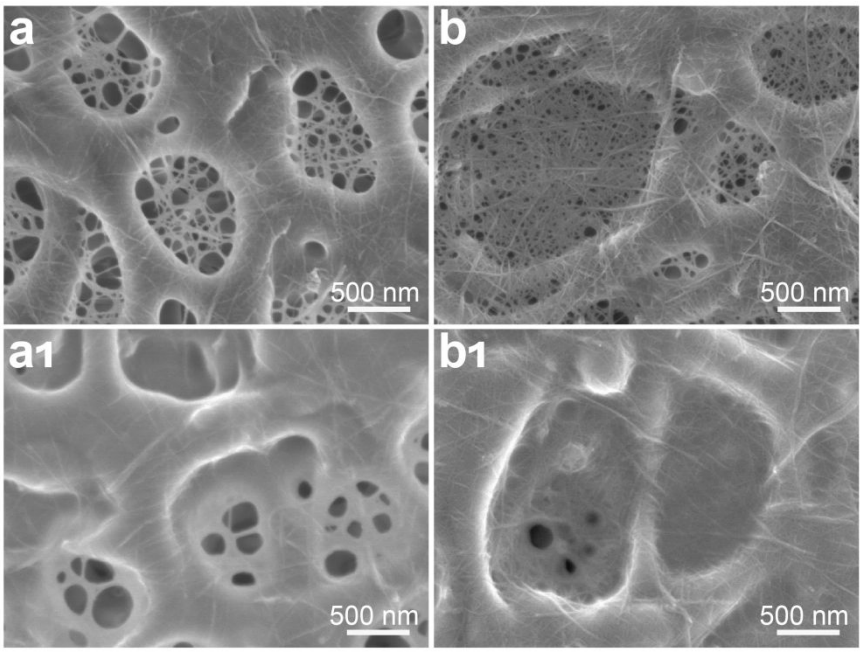

Figure S5. SEM images of SWCNT network films vacuum-filtrated on PES MF membranes with SWCNT density of (a) 0.58 μg cm^{-2} and (b) 1.1 μg cm^{-2}, and correponding SWCNT networks after depositing PEI 600 (a1 and b1). **Note:** The nanopores created by 0.58 μg cm^{-2} and 1.1 μg cm^{-2} SWCNT are not uniform and some of them are too big (pore sizes range from 100 to 400 nm in diameter) for PEI to fill, as suggested by the uncovered pores in Figure S3a1 and b1. The PA/SWCNT NF membranes prepared by these two SWCNT films exhibit low rejections to $MgCl_2$ (Table S1), comfirming the existence of defects in the active layers.

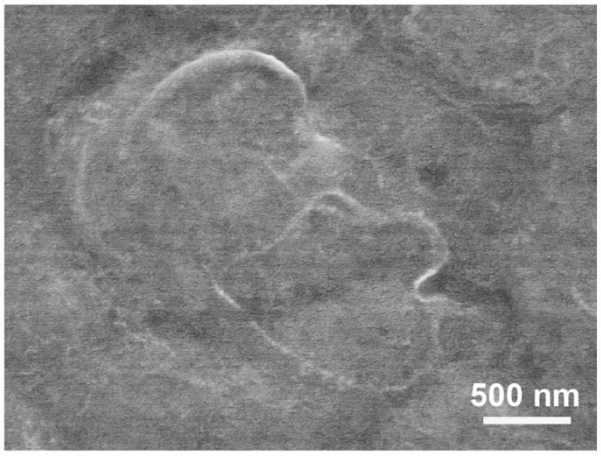

Figure S6. SEM image of lower surface of the PA/SWCNT NF membrane prepared with PEI 70000.

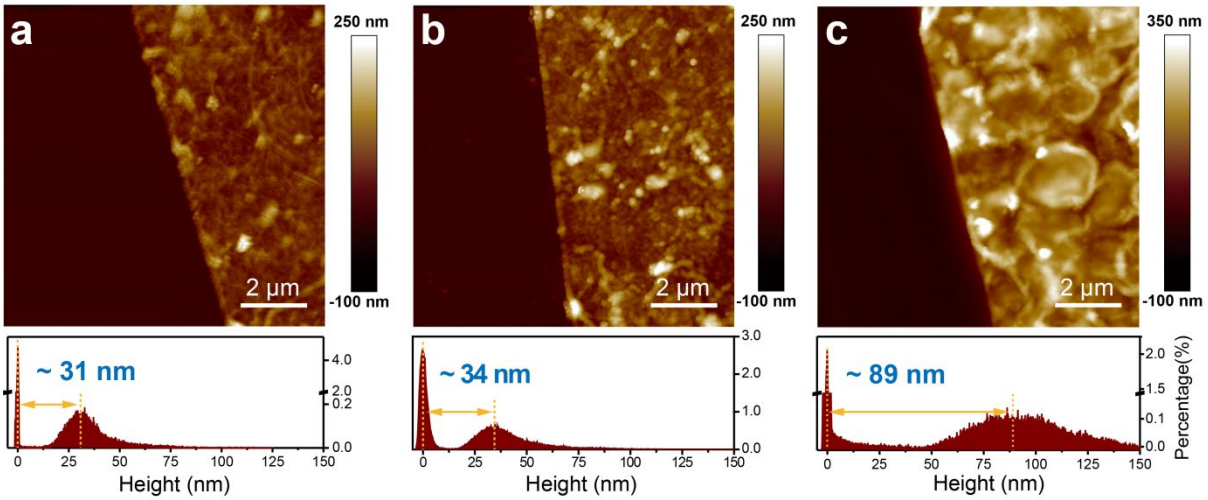

Figure S7. AFM images and corresponding statistical height distributions of (a) pristine SWCNT film, PA/SWCNT active layers prepared with (b) PEI 600 and (c) PEI 70000.

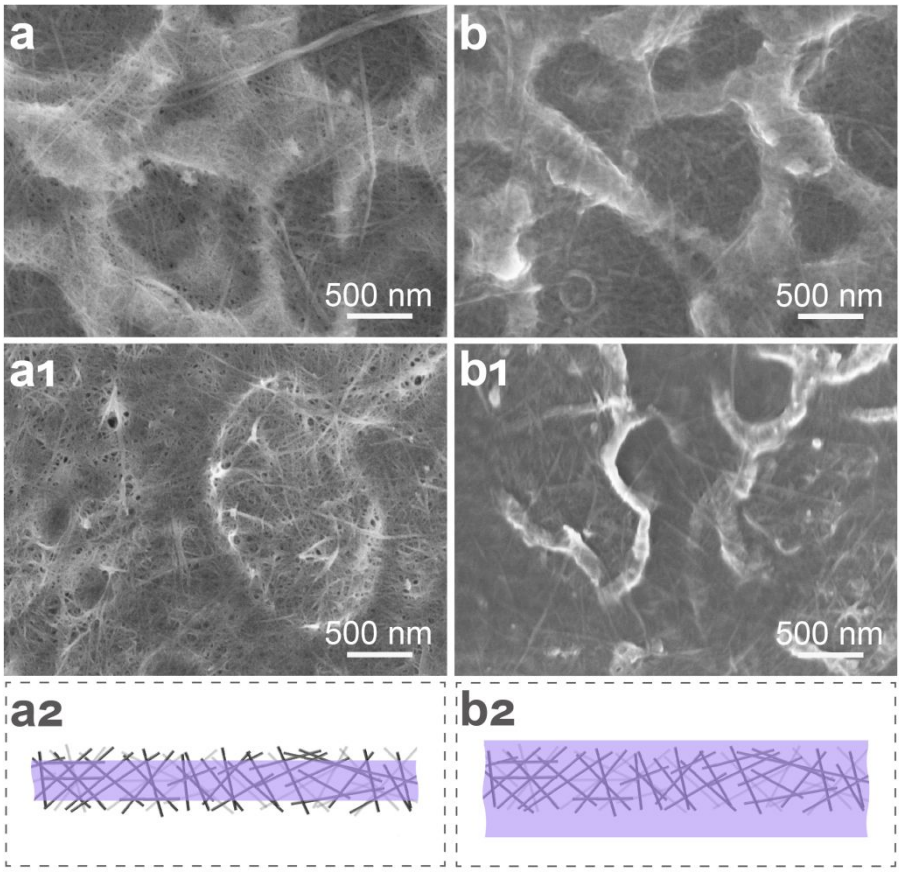

Figure S8. SEM images of PA/SWCNT NF membranes prepared with (a) 0.6 mg ml^{-1} TMC and (b) 6 mg ml^{-1} TMC: (a, b) the upper surfaces and (a1, b1) the corresponding lower surfaces. (a2-d2) Their corresponding schematic diagram showing cross-sectional structures of PA/SWCNT active layers.

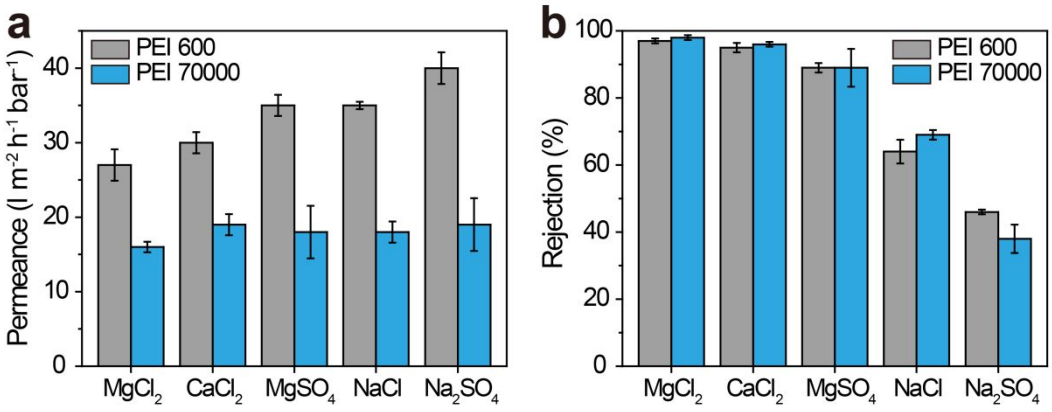

Figure S9. Nanofiltration performance of the PA/SWCNT NF membranes prepared with PEI 600 and PEI 70000: (a) water permeance and (b) rejection to various salts.

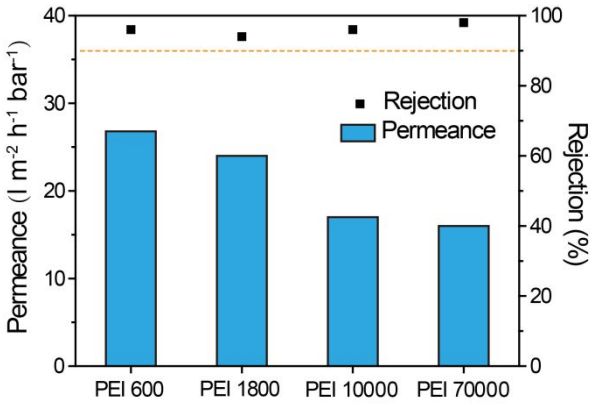

Figure S10. Permeance and rejection of the PA/SWCNT NF membranes prepared with different molecular weight of PEI to 1000 ppm $MgCl_2$.

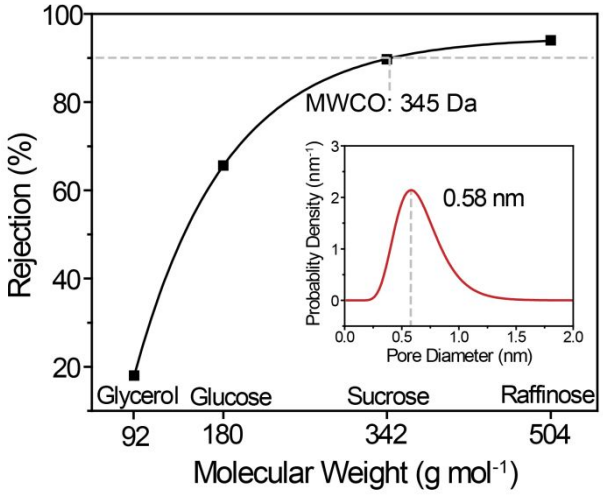

Figure S11. MWCO curve of the PA/SWCNT NF membrane prepared with PEI 70000 and its pore size distribution (insertion).

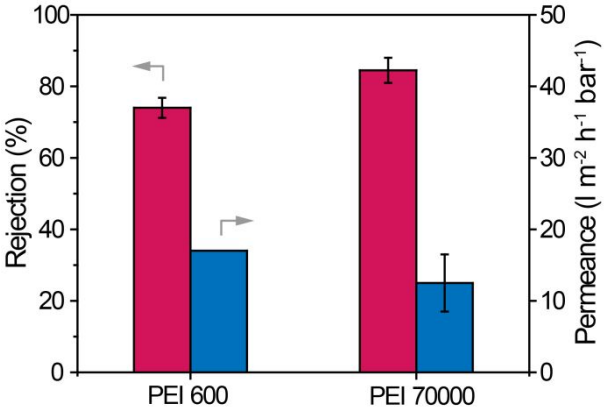

Figure S12. Permeance and rejection of the NF membranes prepared on commercial PES ultrafilration membrane (MWCO of 50,000 Da) with PEI 600 and PEI 70000 to 1000 ppm $MgCl_2$. (PEI concentration: 5 mg ml^{-1}, TMC concentration: 0.6 mg ml^{-1}, reaction time: 1 min).

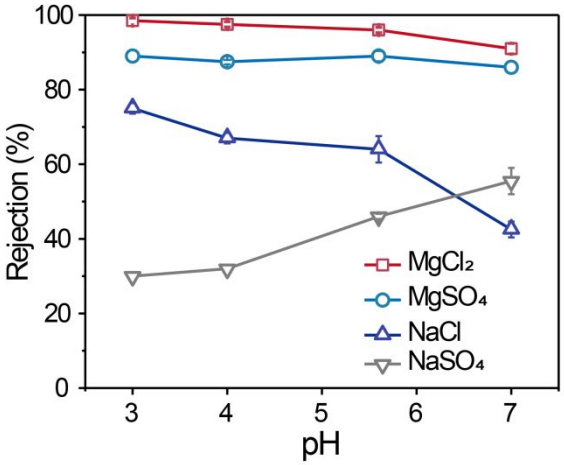

Figure S13. Effect of pH on salt rejections of the PA/SWCNT NF membrane prepared with PEI 600.

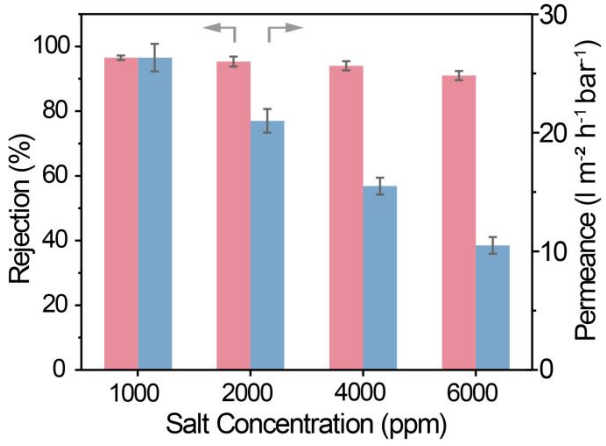

Figure S14. Rejection and permeance of the PA/SWCNT NF membrane prepared with PEI 600 for various concentrations of $MgCl_2$ feed solution.

Supplementary Tables

Table S1. Effect of SWCNT density on the nanofiltration performance of PA/SWCNT NF membranes.

SWCNT density ($\mu g\ cm^{-2}$)	Membrane thickness (nm)	Rejection for $MgCl_2$ (%)	Permeance ($l\ m^{-2}\ h^{-1}\ bar^{-1}$)
0.58	11	73 ± 4	32 ± 3
1.1	20	92 ± 6	30 ± 1
2.3	34	97 ± 1	27 ± 2

Table S2. Size information of PEI 70000 molecules.

PEI MW ($g\ mol^{-1}$)	m ($g\ mol^{-1}$)	n	l (nm)	R_0 (nm)
70000	43	1628	0.36	37.6

Notes: m: molecular weight for each monomer unit, n: number of monomer units in a polymer chain, l: contour length per monomer unit, R_0: root-mean-square end-to-end distance (the size of the polymer coil)

Detailed calculation: For each monomer unit (CH_2CH_2NH) of PEI, there are two C-N bond (bond length of 0.147 nm) and one C-C bond (bond length of 0.154 nm), the bond angles for N-C-C and C-N-C here are supposted to be 109.47° and 107.13°, respctively. The contour length for this nuit can be calculated as:

$$l = 0.154\ \text{nm} * \sin\left(\frac{109.47°}{2}\right) + 0.147\ \text{nm} * \sin\left(\frac{107.13°}{2}\right) * 2 \approx 0.36\ \text{nm}$$

According to freely-jointed chain model, root-mean-square end-to-end distance of a flexible polymer chain can be caculated as:

$$R_0 = \sqrt{< R^2 >} = \sqrt{C_\infty n l^2}$$

where C_∞ is Flory characteristic length. Flory characteristic length of PEI is not found in the literature, we here use the data of poly(ethylene oxide) for estimation, which is 6.7.

Table S3. Chemical components of SWCNT film and PA/SWCNT NF membranes based on deconvolution of C1s XPS spectra.

Membranes	B.E. (eV)	FWHM	Species	Content (%)
SWCNT film	284.4	0.98	C=C	72.5
	285.2	0.98	C-C	17.0
	286.1	1.05	C-O/C-N	7.2
	287.4	1.69	C=O	3.3
PA/SWCNT PEI 600	284.6	1.10	C=C	46.1
	285.3	1.09	C-C	24.2
	286.1	1.21	C-O/C-N	19.8
	287.8	1.28	O-C=O/N-C=O	9.9
PA/SWCNT PEI 70000	284.2	1.05	C=C	28.2
	285.0	1.15	C-C	31.9
	285.8	1.29	C-O/C-N	29.6
	287.6	1.16	O-C=O/N-C=O	10.4