Electronic supplementary information

One-Step Constructed Ultrathin Janus Polyamide Nanofilm with Opposite Charges for Highly Efficient Nanofiltration

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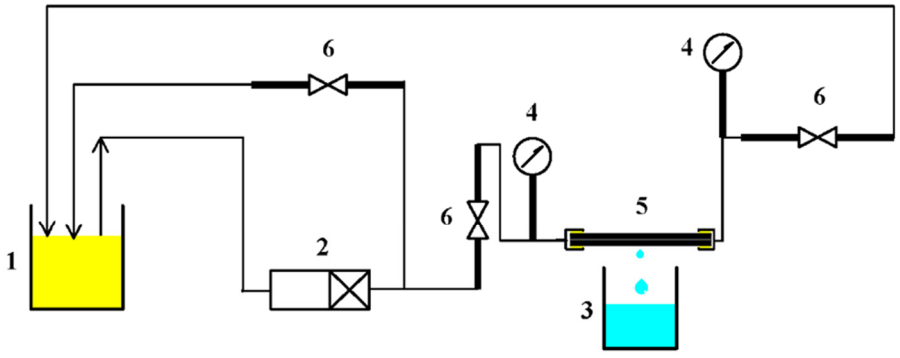

Fig. S1 Schematic diagram of the cross-flow nanofiltration system for hollow fiber modules

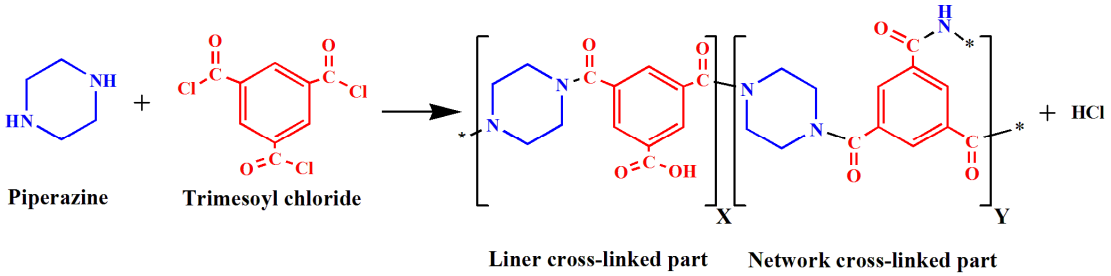

Fig. S2 Interfacial polymerization of PIP and TMC and the resultant polymer with liner cross-linked part and network cross-linked part.

$$O/N = \frac{4X + 3Y}{2X + 3Y} \qquad \textbf{Equation S1}$$

$$DNC = \frac{Y}{X + Y} \times 100\,\% \qquad \textbf{Equation S2}$$

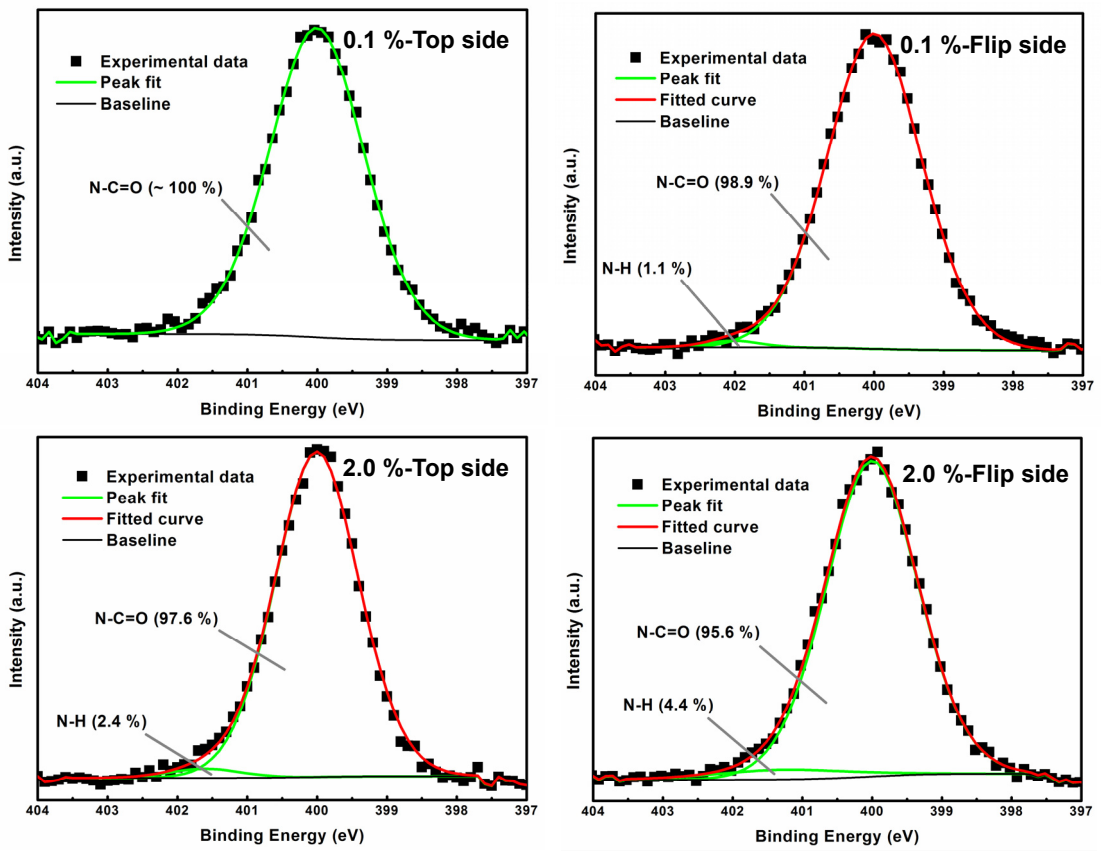

Fig. S3 High-resolution XPS spectra of top side and flip side of free-standing PA nanofilms prepared under PIP concentration of 0.1 % and 2.0 %, respectively. Other prepared conditions for the selected HF-NFMs: TMC: 0.1 %, reaction time: 60 s.

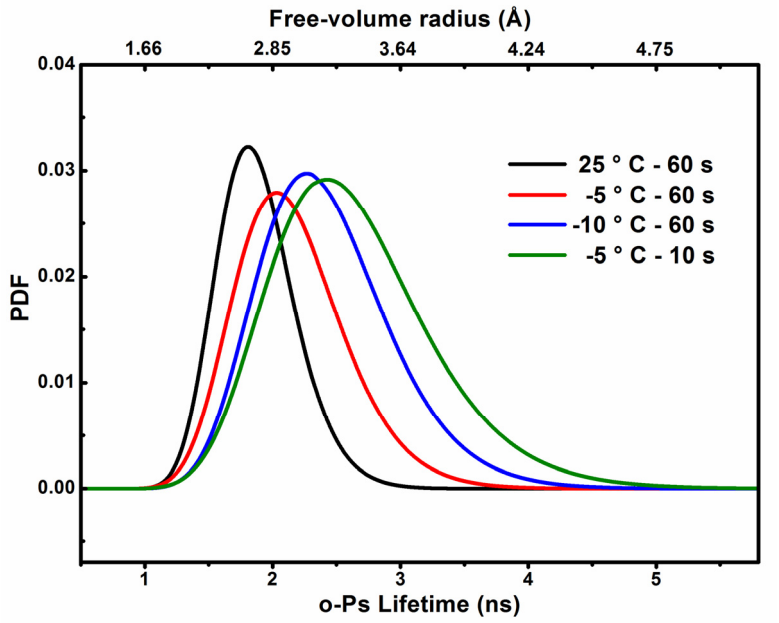

Fig. S4 Mean free-volume radius and o-Ps lifetime distributions of HF-NFMs (other prepared conditions for the selected HF-NFMs: PIP: 1.0 %, TMC: 0.1 %).

Table S1 Parameters involved in the calculation of separating layer thickness

Membranes	E [a] (keV)	ρ [b] (g·cm^{-3})	L (nm)
25 °C-60 s	1.7	1.17	80.7
-5 °C-60 s	1.2	1.05	51.0
-10 °C-60 s	1.0	1.05	38.1
-5 °C-10 s	1.0	1.05	38.1

[a]:The inflection point before the boundary zone between separating layer and porous PVC support (Fig. 4a). [b]:The density of polypiperazine-amide was calculated according to previous studys.[S1]

Table S2. Chemical composition of inner surface of HF-NFMs varied with organic phase temperature

Organic phase temperature	Atomic composition from XPS (%)			O/N	DNC (%)
	C	O	N		
25 °C	73.43	14.75	11.82	1.25	66.9
10 °C	72.74	16.09	11.17	1.44	45.8
0 °C	72.63	16.60	10.77	1.54	36.1
-5 °C	72.50	16.75	10.75	1.56	34.5
-10 °C	72.48	16.80	10.72	1.57	33.7
-15 °C	72.40	16.92	10.68	1.58	32.2

The HF-NFMs were prepared from 1.0 % PIP and 0.1 % TMC for 60 s. Depending on the liner cross-linked (X) and network cross-linked (Y) structure in Fig. S2, the degree of network cross-linking (DNC, %) was calculated based on the following equation S1 and S2.

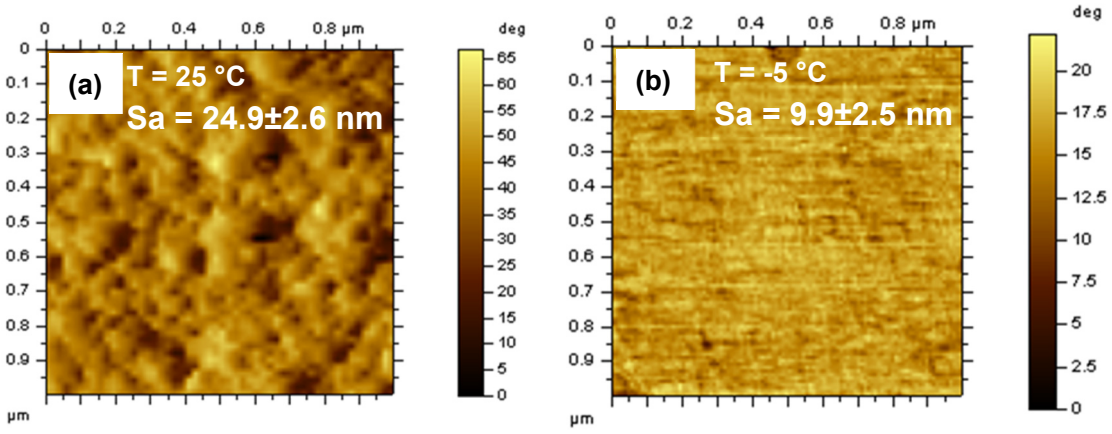

Fig. S5 Phase images of HF-NFMs prepared under organic phase temperature of (a) 25 °C and (b) -5 °C (other prepared conditions for the selected HF-NFMs: PIP: 1.0 %, TMC: 0.1 %, reaction time: 60 s).

Table S3. Inner surface roughness of HF-NFMs prepared under different organic phase temperature

Organic phase temperature	Sa[a] (nm)	Sq[b] (nm)	Sz[c] (nm)
25 °C	24.9 ± 2.6	30.9 ± 2.3	181.7 ± 4.0
10 °C	14.1 ± 0.8	19.9 ± 1.1	133.0 ± 34.0
-5 °C	9.9 ± 2.5	13.1 ± 3.5	84.8 ± 21.4
-10 °C	7.5 ± 0.8	9.6 ± 0.6	69.5 ± 9.9
-15 °C	7.7 ± 0.5	9.7 ± 0.7	70.8 ± 15.0

The HF-NFMs were prepared from 1.0 % PIP and 0.1 % TMC for 60 s. [a] Average roughness. [b] Root mean square roughness. [c] Median peak-to-valley height. 2×2 μm^2 AFM scan sizes were used to calculate the roughness parameters.

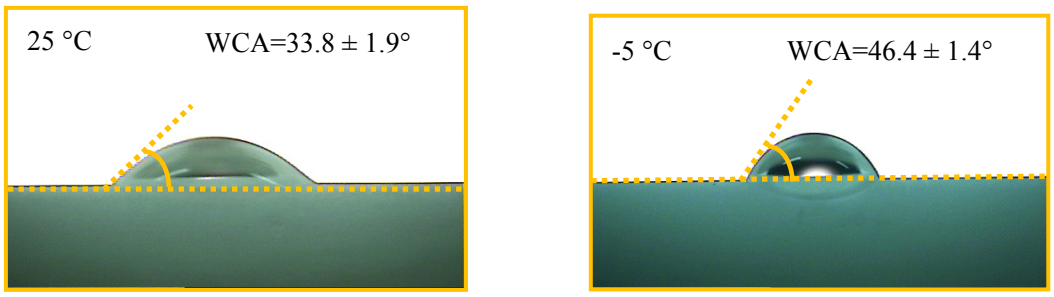

Fig. S6 Water contact angle of inner surface of HF-NFMs fabricated under organic phase temperature of 25 °C and -5 °C (other prepared conditions for the selected HF-NFMs: PIP: 1.0 %, TMC: 0.1 %, reaction time: 60 s).

Table S4. Comparison with other NFMs for desalination

Membranes	Surface charge N/P	$R_{(MgCl2)}$ (%)	$R_{(Na2SO4)}$ (%)	$[R_{(MgCl2)} + R_{(Na2SO4)}]/2$ (%)	Water permeation ($L \cdot m^{-2} \cdot h^{-2} \cdot bar^{-1}$)	Ref.
PIP-TMC/PPESK	N	9.6	99.0	54.3	12.8	S2
PIP-TMC/MWCNTs	N	78.0	95.0	86.5	17.6	S3
PIP-TMC/PD/SWCNTs	N	61.8	95.9	78.8	32.0	S4
PEI-TMC/PES	P	96.7	54.2	75.4	17.0	S5
(PEI+PIP)-TMC/PES	P	96.3	77.4	86.8	18.2	S6
PIP-TMC/(TA+DETA)/PSF	N	70.0	98.0	84.0	10.5	S7
ZrO_2/(PDA+PEI)/HPAN	P	82.0	30.0	56.0	10.0	S8
PIP-mmBTEC/PAN	P	94.9	40.9	67.9	14.6	S9
PIP-TMC/PD/PES	N	12.3	93.5	52.9	11.4	S10
(PDA-MWCNTs) in PEI-TMC/PSF	P	91.5	45.2	68.4	15.3	S11
Dow-Filmtec NF 270	N	60.0	98.0	79.0	13.2	S6
Dow-Filmtec NF 90	N	96.0	98.6	97.3	6.7	S12
Nitto-Denko NTR-7450	N	16.0	92.0	54.0	10.9	S6
Toray UTC20	P	98.0	93.0	95.5	10.2	S6
PIP-TMC/aminated PVC	N-P	99.0	96.0	97.5	7.1	S1
PIP-TMC/CNC/PES	N	15.5	97.7	56.6	34.0	S13
PAA/PEI/PDA/PA	N-P	97.2	98.3	97.7	5.5	S14
This work 1	N-P	97.0	82.0	89.5	18.6	--
This work 2	N-P	97.1	93.2	95.2	16.5	--
This work 3	N-P	98.6	94.3	96.5	15.2	--
This work 4	N-P	98.0	96.5	97.3	12.9	--

N: negatively charged; P: positively charged; N-P: dually charged separating layer

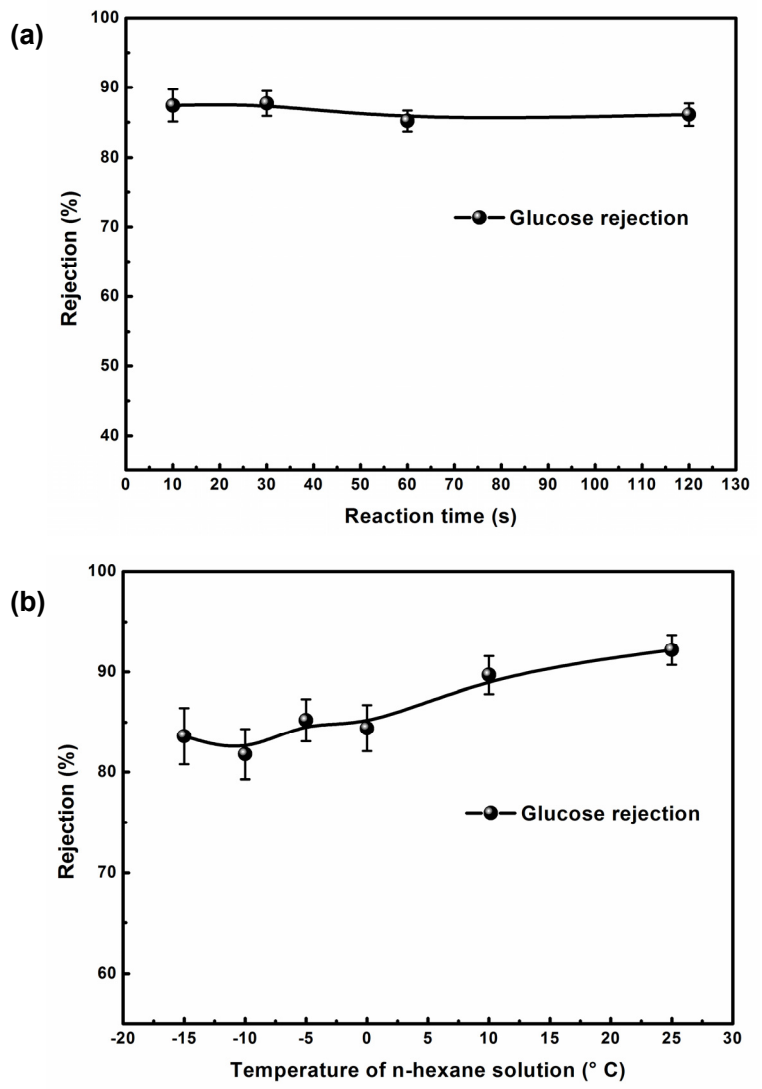

Fig. S7 Variation of glucose (180 Da) rejection of HF-NFMs prepared with different reaction time and organic phase temperature. Herein, 500 mg·L^{-1} glucose aqueous solution was used as the feed. Generally speaking, rejection to neutral molecules can be used to estimate the pore size of NFMs. Fig. S7 shows the glucose rejection almost constant with the increasing of reaction time while decrease with the decrease of organic phase temperature. Other prepared conditions of HF-NFMs involved in Fig. S7a: PIP: 1.0 %, TMC: 0.1 %, organic phase temperature: -5 °C. Other prepared conditions of HF-NFMs involved in Fig. S7b: PIP: 1.0 %, TMC: 0.1 %, reaction time: 60 s.

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