ARTICLE

Highly crosslinked, chlorine-tolerant polymer network entwined graphene oxide membrane for water desalination

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Seungju Kim[a], Xiaocheng Lin[a], Ranwen Ou[a], Huiyuan Liu[a], Xiwang Zhang[a], George P. Simon[b], Christopher D. Easton[c], and Huanting Wang[*a]

Supplementary Information

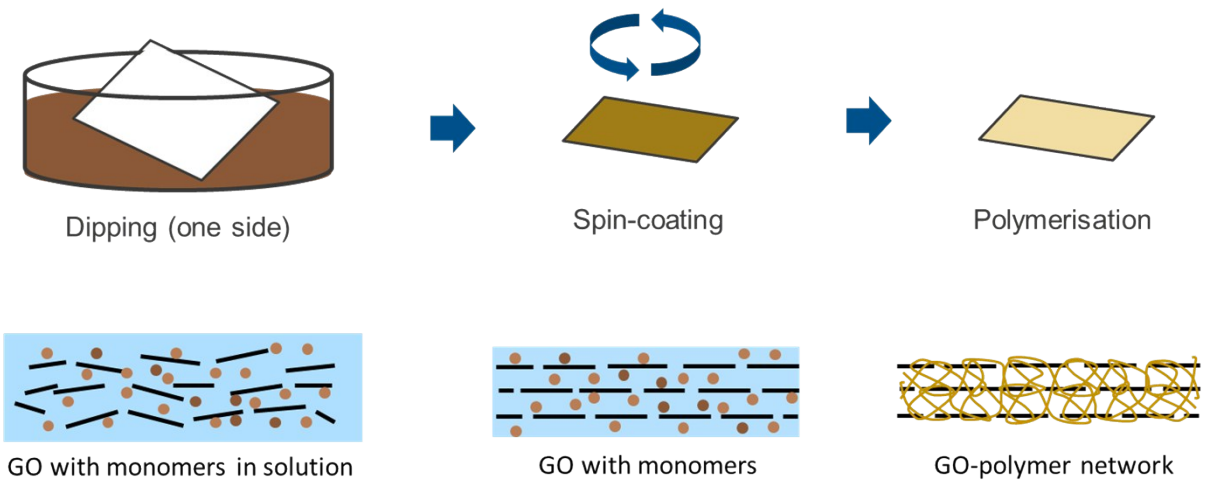

Fig. S1 Schematic representation of fabrication of polymer network entwined GO thin-film composite membrane.

[a] *Department of Chemical Engineering, Monash University, VIC 3800, Australia. E-mail: huanting.wang@monash.edu*
[b] *Department of Materials Science and Engineering, Monash University, VIC 3800, Australia.*
[c] *CSIRO Manufacturing, Bayview Ave, Clayton, VIC 3168, Australia.*
† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Table S1 Detailed quantities of components in the precursor solution for spin-coating

Samples	Monomers (mg)			Water (ml)	GO (mg)	GO conc. (mg/ml)	GO/polymer ratio (wt%)
	NIPAM	MBA	APS				
GO-P61	38	38	7	10	3.4	0.34	4.5
GO-P65					4.8	0.48	6.3
GO-P72					9.5	0.95	12.5
GO-P79					19	1.9	25.0
GO-P87					28.5	2.85	37.5
GO-P95					38	3.8	50.0

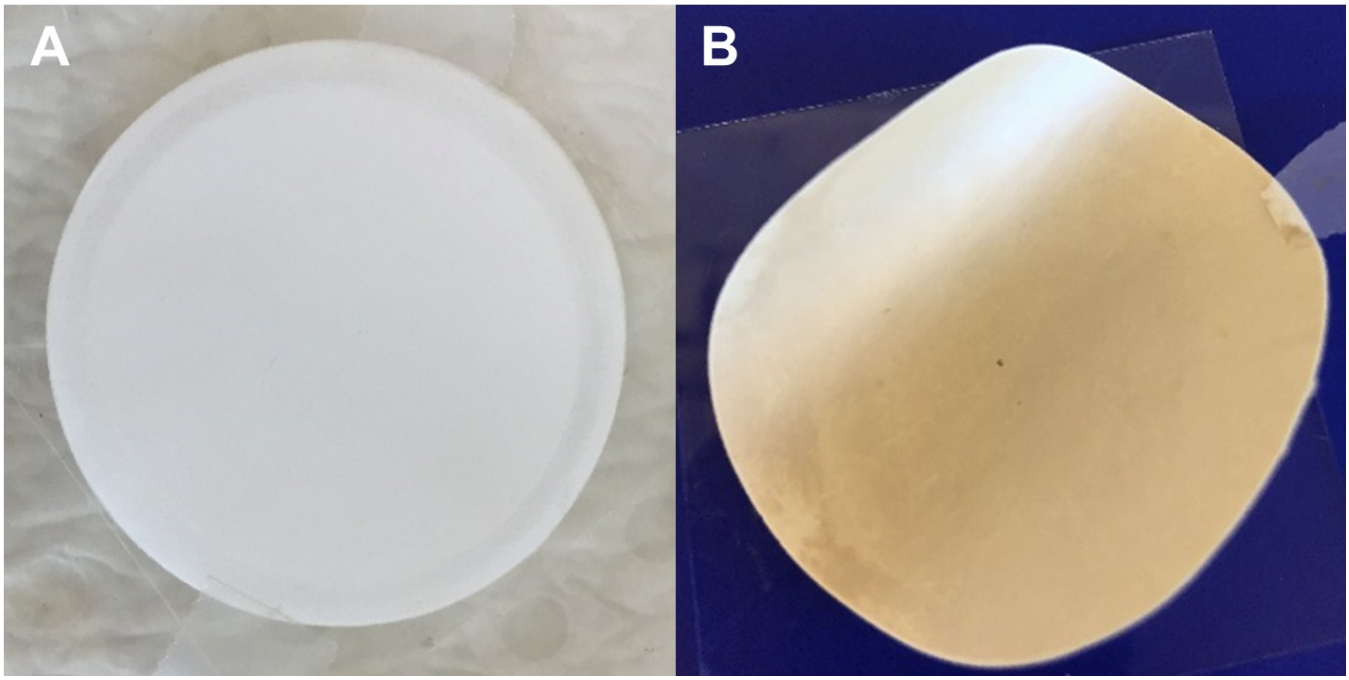

Fig. S2 Photos of (A) a Nylon substrate, and (B) a GO-polymer composite membrane (GO-P61).

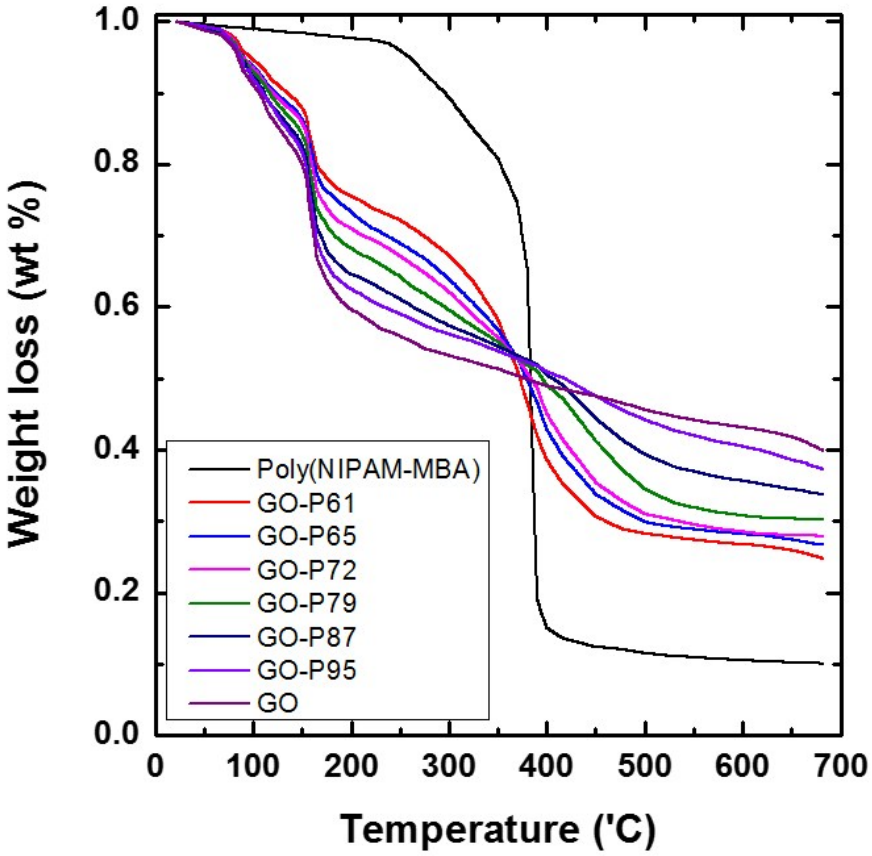

Fig. S3 Thermogravimetric analysis (TGA) curves of GO-polymer composites with different GO/polymer ratios.

Poly(*N*-isopropylacrylamide-*co*-*N*,*N'*-methylene-bis-acrylamide) are thermally stable until around 250 °C and dramatically decomposed after 350 °C. Otherwise, there is a serious weigh loss between 100 °C and 200 °C on GO from a decomposition of hydroxyl groups on GO. GO-polymer ratio was confirmed by comparison of weight change between 100 °C and 250 °C.

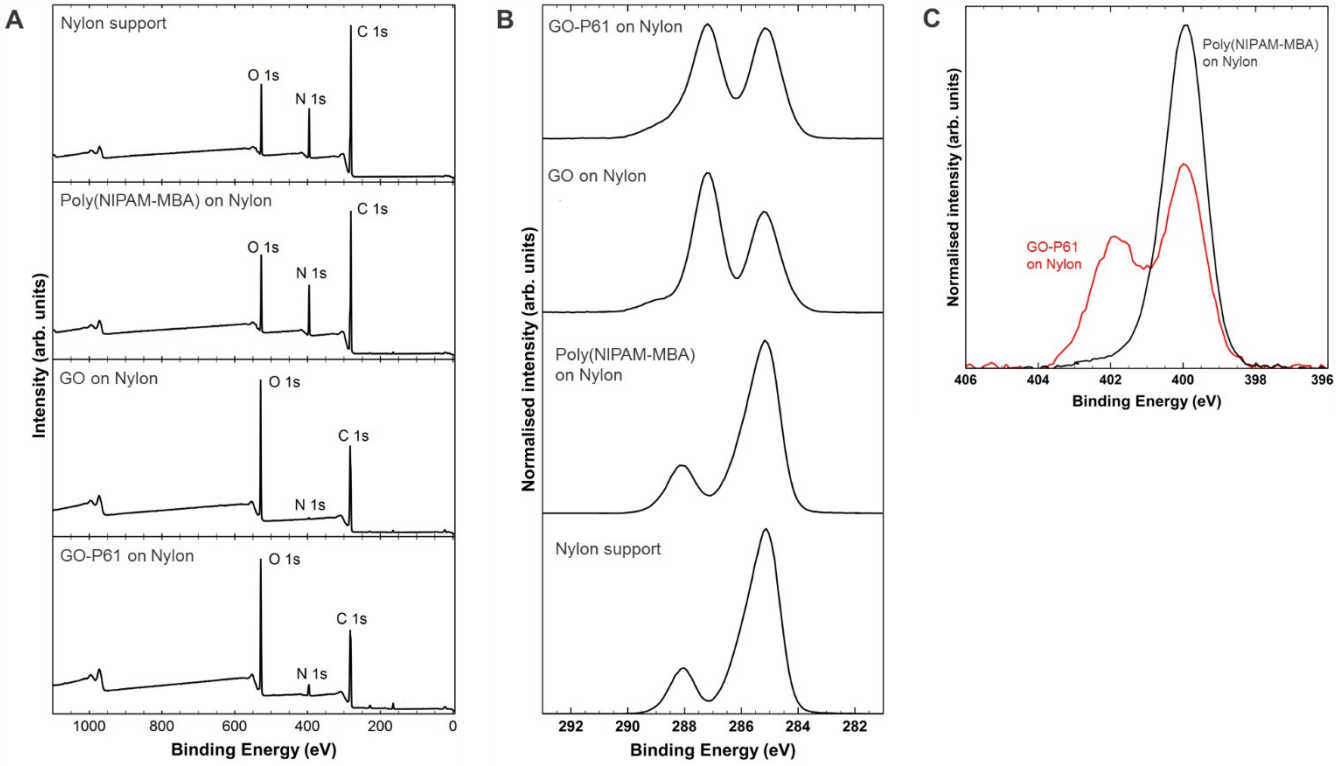

Fig. S4 X-ray photoelectron spectroscopy (XPS) spectra (a) survey spectrum series, (b) selected, representative C 1s spectra of untreated and modified Nylon support samples, and (c) selected, representative N 1s spectra overlay of polymer coated Nylon filter with (GO-P61) and without GO (poly(NIPAM-MBA)).

XPS analysis confirms GO on Nylon as the N signal is suppressed significantly and N/O ratio has dropped as compared with raw Nylon support.[1] In the C 1s spectra (**Fig. S4B**), spectra are normalised to total peak area and charge corrected using a binding energy reference value of 285 eV for aliphatic hydrocarbon. Intensity in the region 288 eV is associated with amides, as expected for the Nylon support and poly(NIPAM-MBA) coated Nylon support samples, where the peak shape is characteristic of a polyamide. The introduction of intensity in the region of 287 eV for the GO treated samples is associated with C-O.[2] For the N 1s spectra (**Fig. S4C**), the addition of GO to the poly(NIPAM-MBA) results in intensity in the region 402 eV, which is associated with N+ groups; this suggests there is a charge interaction between the PNIPAM and GO.[3]

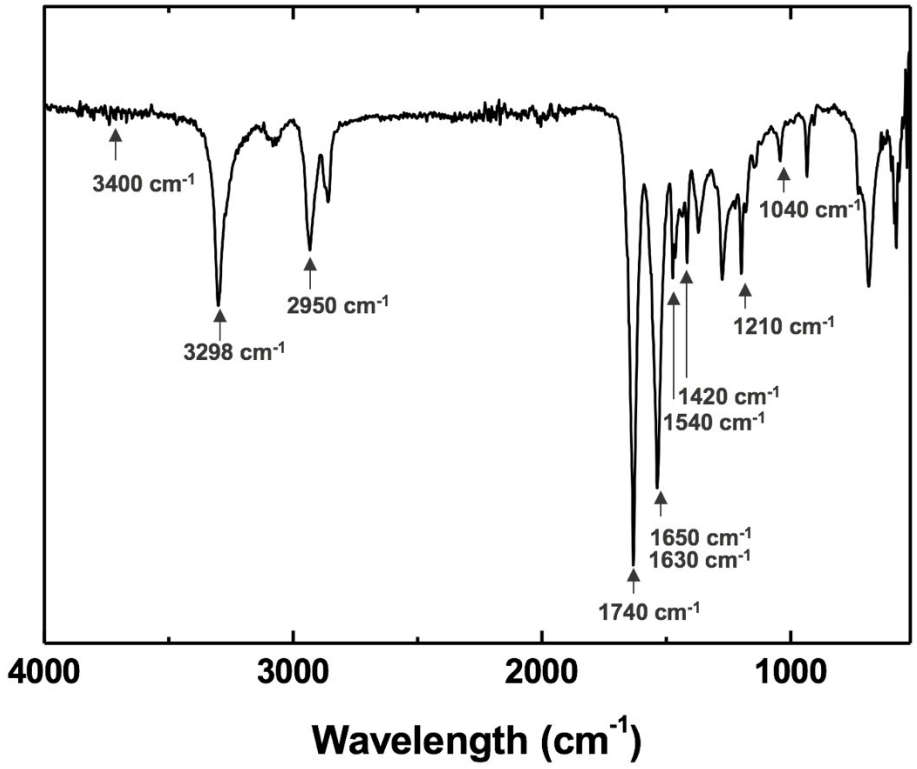

Fig. S5 Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectrum of a GO-polymer thin-film composite membrane (GO-P61).

ATR-FTIR spectrum of a GO-polymer shows combined characteristics of GO and poly(NIPAM-MBA). The main peaks are as follows: 3298 cm^{-1} (secondary amide N-H stretching), 2950 cm^{-1} (-CH_3 asymmetric stretching), 1740 cm^{-1} (secondary amide C=O stretching, 1650 cm^{-1} (secondary amide C=O stretching, aka amide I bond), and 1540 cm^{-1} (C-N stretching) for poly(NIPAM-MBA).[4, 5] 3400 cm^{-1} (O-H stretching), at 1630 cm^{-1} (skeletal vibrations from unoxidized graphitic domains), 1420 cm^{-1} (C=C aromatic ring) 1210 cm^{-1} (C-O-C stretching), and 1040 cm^{-1} (C-O stretching) for GO.[5, 6] GO peaks are relatively weak as compared with poly(NIPAM-MBA) because of coverage of poly(NIPAM-MBA).

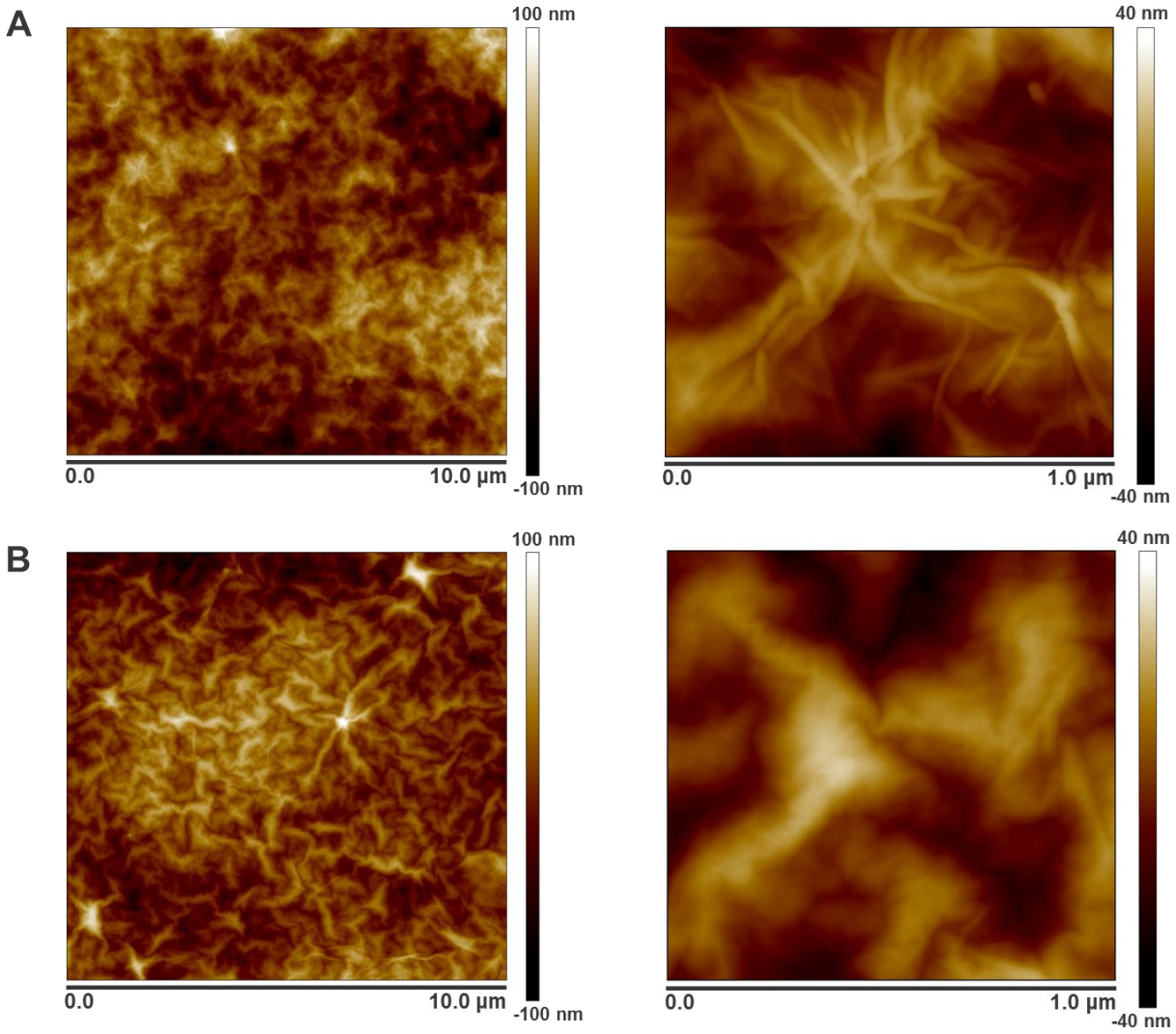

Fig. S6 2D AFM images of (A) a GO-polymer thin-film composite membrane (GO-P61), and (B) a layered GO membrane prepared by spin-coating.

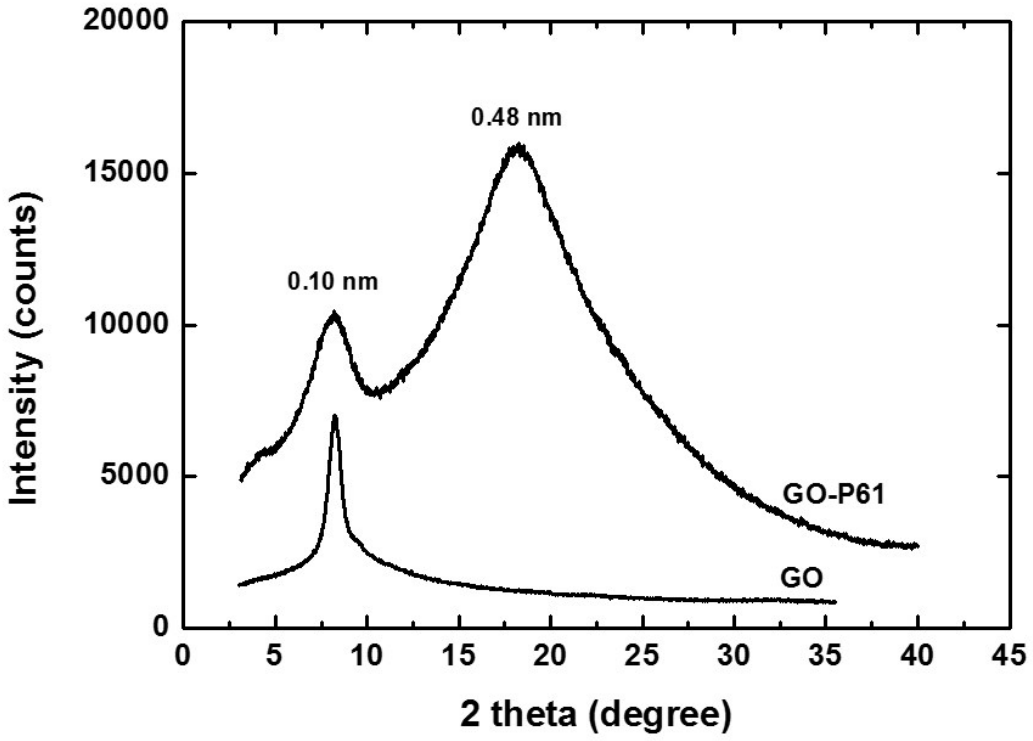

Fig. S7 XRD patterns of a GO and a GO-polymer thin-film composite membrane (GO-P61).

The d-spacing values for the peaks at 8.5° and 18.0° were calculated using Bragg's equation to be 1.04 nm and 0.48 nm, respectively. Because poly(NIPAM-MBA) is amorphous, the d-spacing values should correspond to the interlayer spacing of GO nanosheets. The weak peak at 8.5° is similar to that observed in the pure GO laminate.[7]

* FO performances characterization

The water flux (J_w, L m^{-2} h^{-1}) was calculated by:

$$J_w = \frac{\Delta w}{s\ t} \quad (1)$$

where Δw (L) is the volume change of the feed solution, s (m^2) is the effective membrane area and t (h) is the filtration time.

The reverse salt flux (J_s, g m^{-2}, h^{-1}) was calculated by

$$J_s = \frac{C_t V_t - C_0 V_0}{s\ t} \quad (2)$$

where C_0 (g/L) and V_0 (L) are the initial solute concentration and the initial volume of the feed, respectively, while C_t (g/L) and V_t (L) are the solute concentration and the volume of the feed over a running time t (h). The solute concentration of the feed solution was determined from the conductivity of the solution.

The FO salt rejection (%) was calculated by

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 = \left(1 - \frac{J_{s,p}/J_{w,p}}{C_f}\right) \times 100 \quad (3)$$

where C_p (g/L) and C_f (g/L) are the salt concentration at permeate and feed.

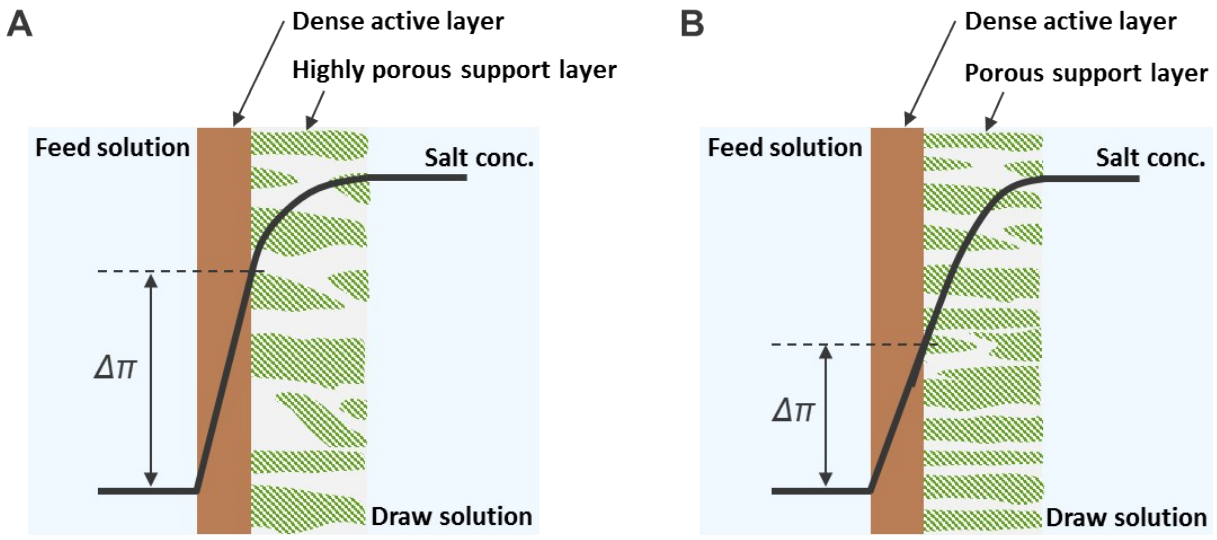

Fig. S8 Osmotic pressure difference of FO composite membranes (A) when a highly porous support was used, and (B) when a less porous support was used.

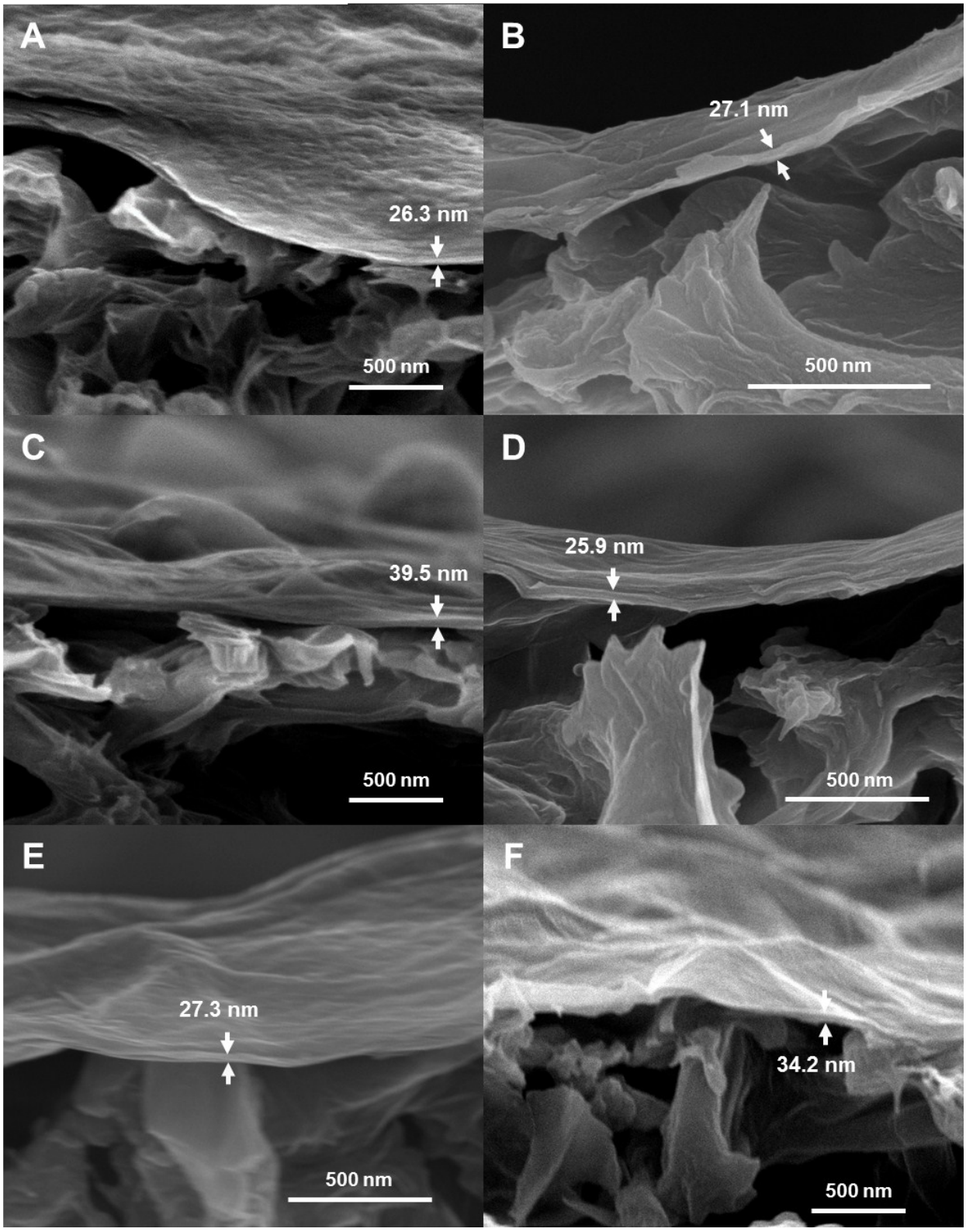

Fig. S9 Cross-sectional SEM images of GO-polymer composite membranes (A) GO-P61, (B) GO-P65, (C) GO-P72, (D) GO-P79, (E) GO-P87, and (F) GO-P95.

References

1 1. G. Beamson and D. Briggs, *Molecular Physics*, 1992, **76**, 919-936.
2 2. D. E. Lobo, P. C. Banerjee, C. D. Easton and M. Majumder, *Adv. Energy Mater.*, 2015, **5**.
3 3. C. D. Easton, A. J. Bullock, G. Gigliobianco, S. L. McArthur and S. MacNeil, *J. Mater. Chem. B*, 2014, **2**, 5558-5568.
4 4. Y. Cui, C. Tao, Y. Tian, Q. He and J. Li, *Langmuir*, 2006, **22**, 8205-8208.
5 5. T. A. Saleh and V. K. Gupta, *Separation and Purification Technology*, 2012, **89**, 245-251.
6 6. Y. Xu, H. Bai, G. Lu, C. Li and G. Shi, *J. Am. Chem. Soc.*, 2008, **130**, 5856-5857.
7 7. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806-4814.