Electronic Supplementary Information

Ultrastable sandwich graphene oxide hollow fiber membranes with confined interlayer spacing

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Experimental

Preparation of GO suspension

A modified Hummer's method was applied for preparing graphite oxide. Graphite powders and $NaNO_3$ were put into concentrated H_2SO_4 gradually. An ice bath was employed to keep the temperature. $KMnO_4$ was extremely slowly dispersed into the above mixture. After 2-h reaction, the suspension was treated at 35 °C for 1 h. Then the suspension was diluted with plenty of deionized water and heated at 98 °C for 40 min. The product was treated by H_2O_2 solution (30%), washed by dilute HCl aqueous solution and deionized water, and dried for use. The GO suspension with concentration of 1.0 mg mL^{-1} was prepared by adding graphite oxide in deionized water. The exfoliation of GO was performed by ultrasonic treatment. The unexfoliated graphite oxide was removed by centrifugation at 4000 rpm.

Preparation of SGO hollow fiber membranes

PVDF, NPVDF and PES hollow fibers were used as substrates for fabrication of GO membranes. Ammoniation was performed by immersing and thermal treating the PVDF hollow fiber in ammonia at 150 °C for 20 h. The modified NPVDF hollow fiber was washed by water and ethanol for several times to remove unreacted ammonia, and dried at room temperature for use. The GO hollow fiber membrane was fabricated by vacuum filtration. The prepared GO suspension was diluted to 50 μg mL^{-1} by deionized water. One end of the hollow fiber was sealed by epoxy resins; the other end was connected with polyurethane tube for vacuum suction. The fiber was immersed in the GO suspension for vacuum filtration. After filtering out for 8.0 mL water, the formed GO

membrane was taken out carefully. The coating solution was prepared by adding PSF in DMF solvent (10 wt%) and stirring at room temperature for 24 h. In order to remove air bubbles, the solution was stood without stirring for 12 h. For fabrication of the SGO-D hollow fiber membrane, the GO membrane was totally dried at 50 °C for 12 h and soaked in the prepared PSF solution for 5 s. Then the GO hollow fiber with PSF solution was immerged in deionized water for formation of porous PSF coat. After 2-min immersion, the hollow fiber was transferred to a fresh water bath and maintained for 3 h. Finally, the prepared SGO-D hollow fiber membrane was dried at 50 °C for use. The fabrication of the SGO-W hollow fiber was similar to that of the SGO-D membrane, except the totally drying procedure of GO membrane. The wetted GO hollow fiber after vacuum filtration was heated at 50 °C for 10 min. Then the heated GO hollow fiber filled with filtered water was directly immerged into the PSF solution. Because the filtered water in tube side served as bore coagulant, the water in hollow fiber and polyurethane tube reduced during PSF immersion. After soaking for 5 s, the PSF-coated hollow fiber membrane was soaked in deionized water and dried as like the fabrication of SGO-D hollow fiber membrane. The PSF/PES hollow fiber was prepared as like that of the SGO-W membrane. The PES hollow fiber was filled with deionized water by vacuum filtration. Then the PES hollow fiber was heated at 50 °C for 10 min, immerged into PSF solution and deionized water, and dried, sequentially.

Desalination performance

Self-made dead-end filtration equipment was employed to evaluate the desalination performance of the prepared hollow fiber membranes. The hollow fiber connected with polyurethane tube was sealed into feed container (500 mL) by epoxy resins. The salt (NaCl, $MgCl_2$, Na_2SO_4 and $MgSO_4$)

solution with different concentrations (500, 1000, 1500 and 2000 mg L^{-1}) was poured into the container. The outer surface of the hollow fiber was exposed to the salt solution and used for calculating the effective membrane area. The tube side of the hollow fiber was the permeate side. The feed pressure was provided and controlled by nitrogen cylinder. After running stably, the permeate solution was collected and recorded. The salt concentration was measured by a conductivity meter. The permeation data of three membrane samples were recorded to obtain the average permeance, rejection and related standard deviations. Water permeance (L m^{-2} h^{-1} bar^{-1}) was calculated based on the permeate volume, membrane area, permeation time and applied feed pressure. Rejection was calculated based on the salt concentrations of feed and collected solutions.

Characterizations

A scanning electron microscope (Ultra-55, Zeiss Co.) with accelerating voltage of 5 kV was applied to observe the morphology of the prepared hollow fiber membranes. The sample was freeze-fractured in liquid nitrogen to maintain the cross-sectional morphology. An ultrathin gold layer was coated on the sample to minimize the charging effect. The interlayer spacing of GO membranes was investigated by X-ray diffractometer (D2 Phaser, Bruker CO.) at 30 kV and 10 mA. For characterization of the wetted sample, the dried sample was immersed in excessive deionized water drops for 1 h.

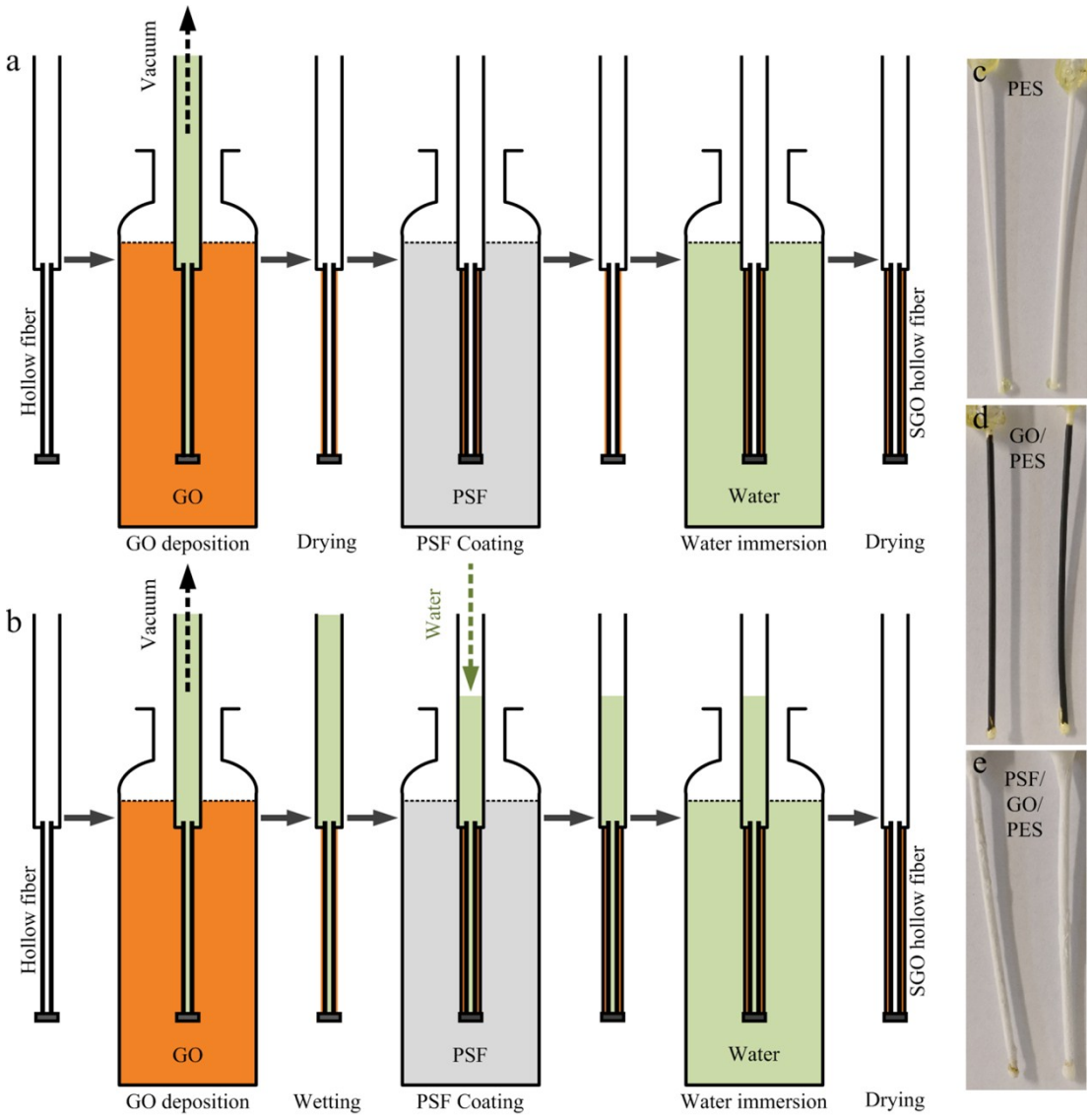

Fig. S1 Preparation of SGO membranes. (a) The schematic of preparation of the SGO-D hollow fiber membranes. GO, PSF and water are presented in brown, gray and green. (b) The schematic of preparation of the SGO-W hollow fiber membranes. Photographs of (c) the PES hollow fiber, (d) the GO/PES hollow fiber and (e) the SGO-W/PES hollow fiber.

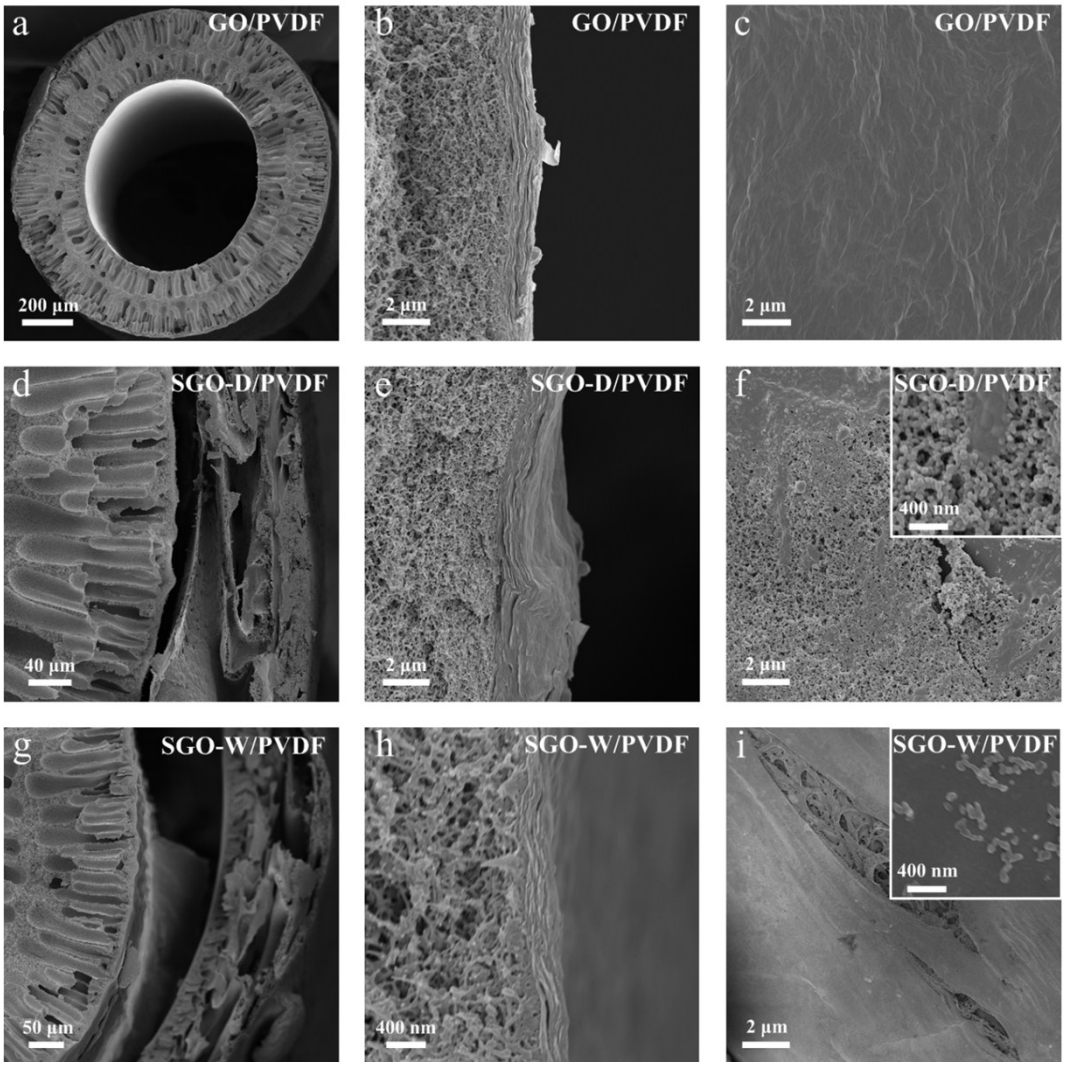

Fig. S2 SEM images of SGO/PVDF membranes. (a-c) SEM images of the GO/PVDF hollow fiber membrane, (a,b) cross-sectional view and (c) outer surface. (d-f) SEM images of the SGO-D/PVDF hollow fiber membrane, (d,e) cross-sectional view and (f) outer surface. (g-i) SEM images of the SGO-W/PVDF hollow fiber membrane, (g,h) cross-sectional view and (i) outer surface. The SGO-D/PVDF and SGO-W/PVDF membranes showed void gaps between GO layer and PSF coat. The PSF coat of the SGO-D/PVDF membrane had inner macroporous structure and outer dense/fingerlike morphology. The PSF coat of the SGO-W/PVDF membrane had inner dense/fingerlike structure, outer macroporous morphology and dense surface skin.

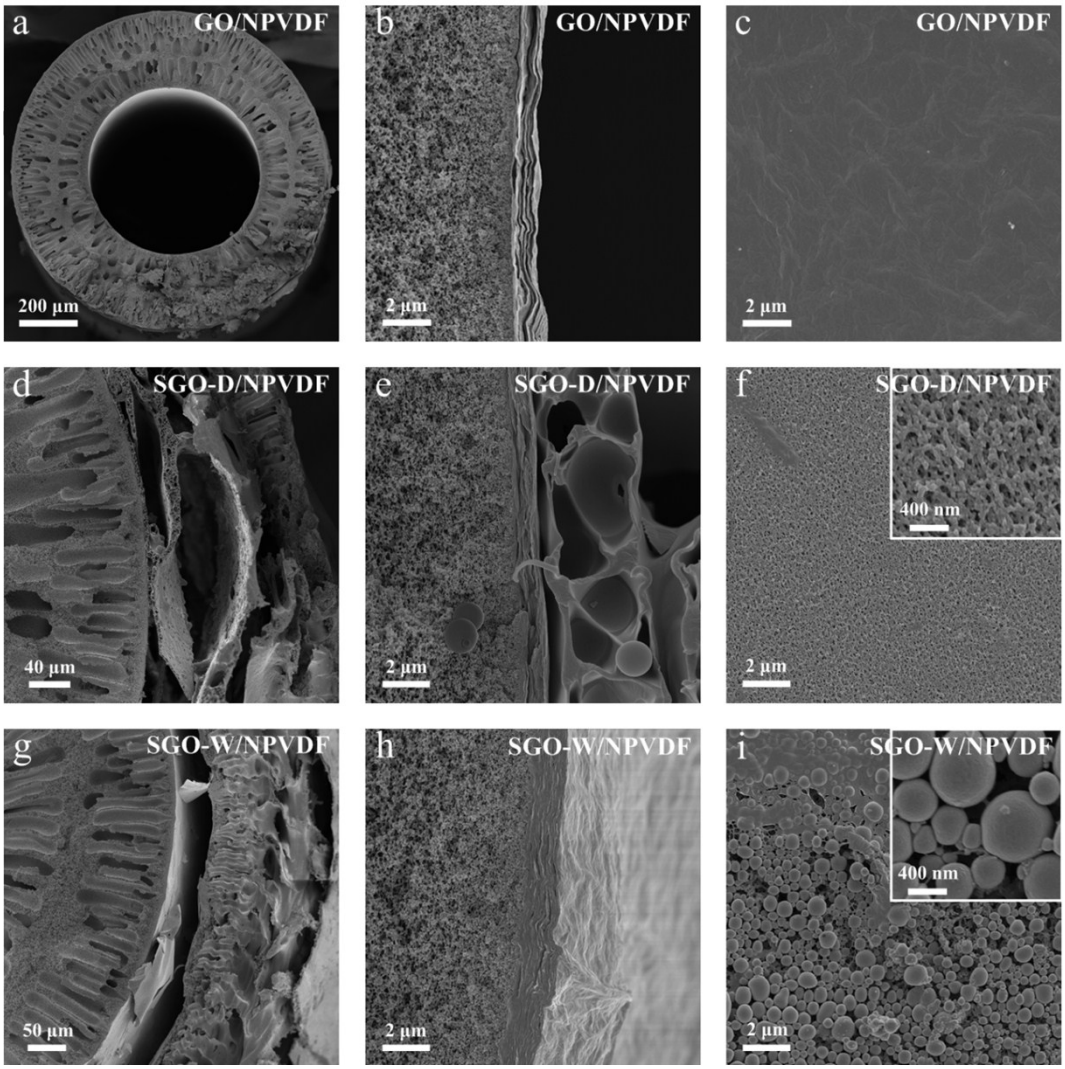

Fig. S3 SEM images of SGO/NPVDF membranes. (a-c) SEM images of the GO/NPVDF hollow fiber membrane, (a,b) cross-sectional view and (c) outer surface. (d-f) SEM images of the SGO-D/NPVDF hollow fiber membrane, (d,e) cross-sectional view and (f) outer surface. (g-i) SEM images of the SGO-W/NPVDF hollow fiber membrane, (g,h) cross-sectional view and (i) outer surface. The SGO-D/NPVDF and SGO-W/NPVDF membranes showed obviously interfacial gaps. The PSF coat of the SGO-D/NPVDF membrane had inner macroporous and outer dense/fingerlike morphologies. The PSF coat of the SGO-W/NPVDF membrane had inner dense/fingerlike structure, outer macroporous morphology and granular surface.

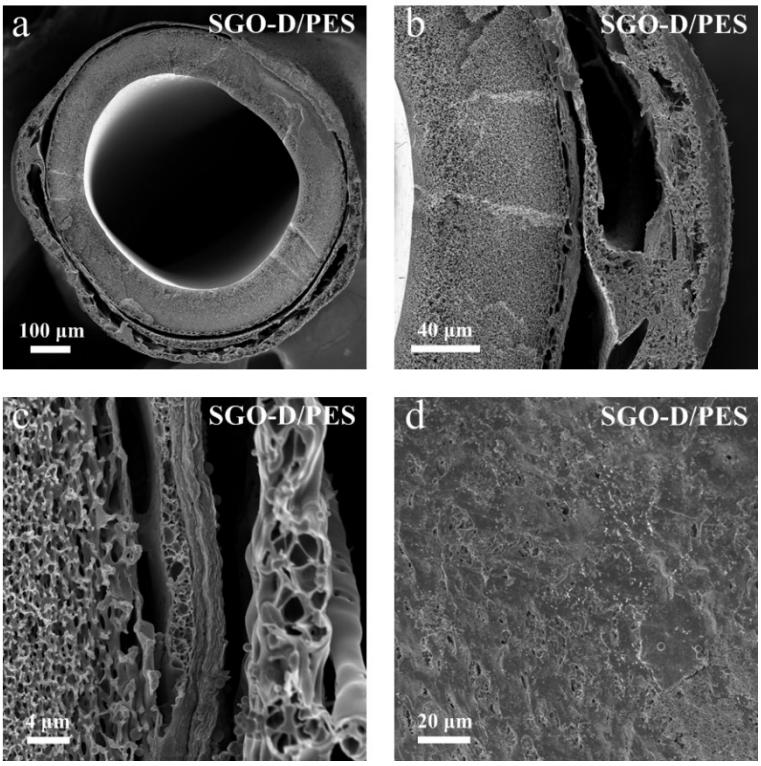

Fig. S4 SEM images of the SGO-D/PES membrane. (a-c) Cross-sectional view of the SGO-D/PES hollow fiber membrane. (d) Top view outer surface of the SGO-D/PES hollow fiber membrane. The PSF coat had inner macroporous structure and outer dense/fingerlike morphology.

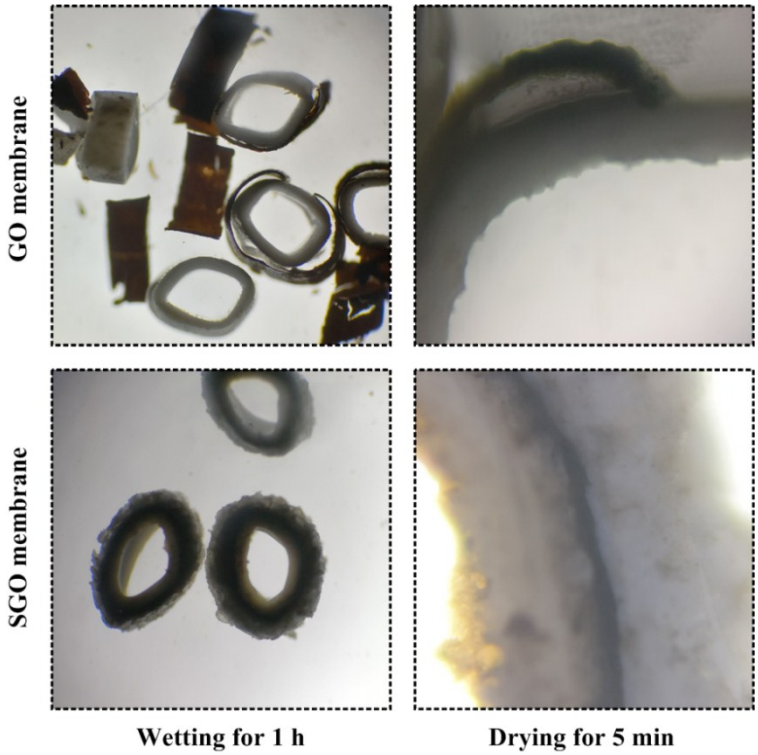

Fig. S5 Optical microscopy images. Optical microscopy images of the 1-h wetted and 5-min dried GO/PES and SGO-W/PES hollow fiber membranes. The drying process was performed at room temperature. Compared with the image displayed in Fig. 2a, the wetted GO layer of the GO/PES hollow fiber shrunk rapidly after sample drying.

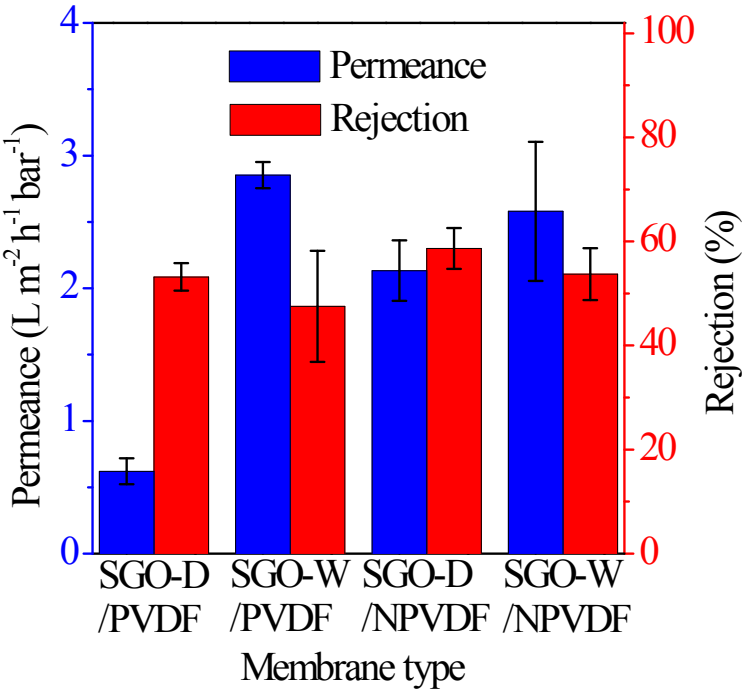

Fig. S6 Desalination performance of various SGO hollow fiber membranes for NaCl solution.

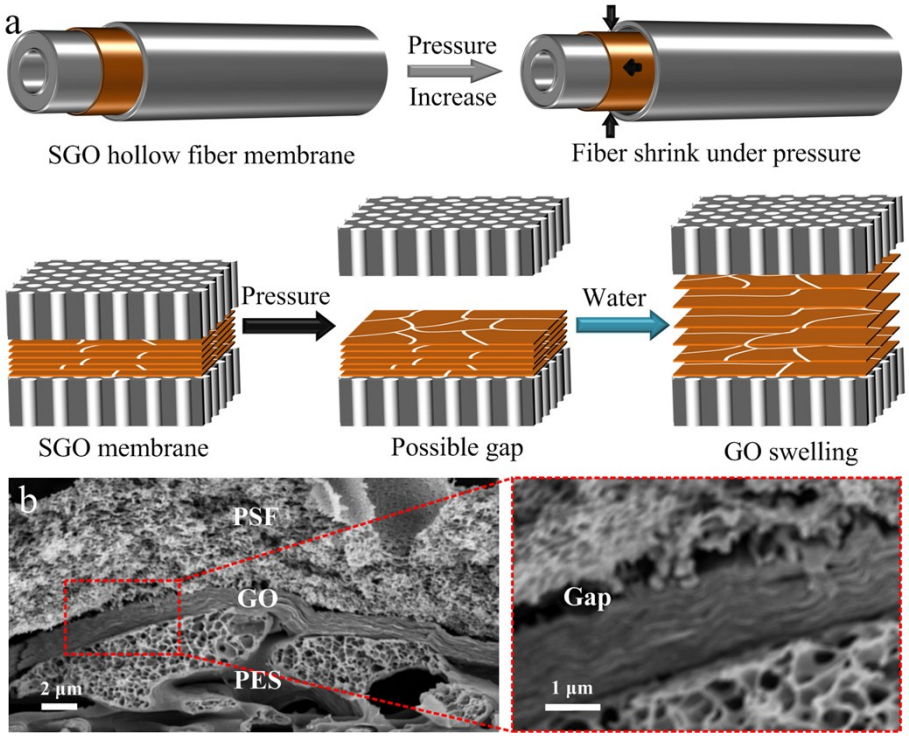

Fig. S7 (a) Possible mechanism of the poor rejection of the SGO-W/PES hollow fiber membrane under high feed pressure. (b) SEM images of SGO-W/PES membrane after filtration with high pressure. The gap between PSF coat and GO layer ocurred after filtration.

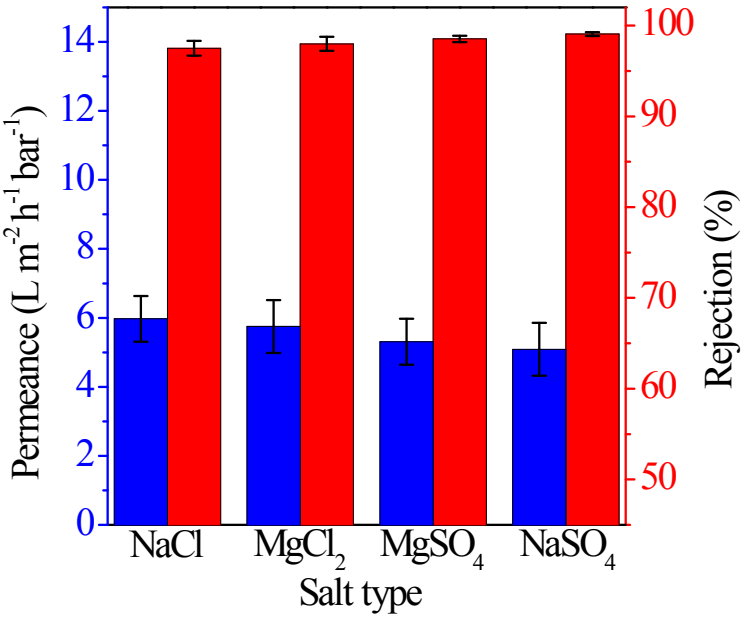

Fig. S8 Permeance and rejection of various salt solutions through the SGO-W/PES hollow fiber membrane with feed pressure of 1.0 bar.

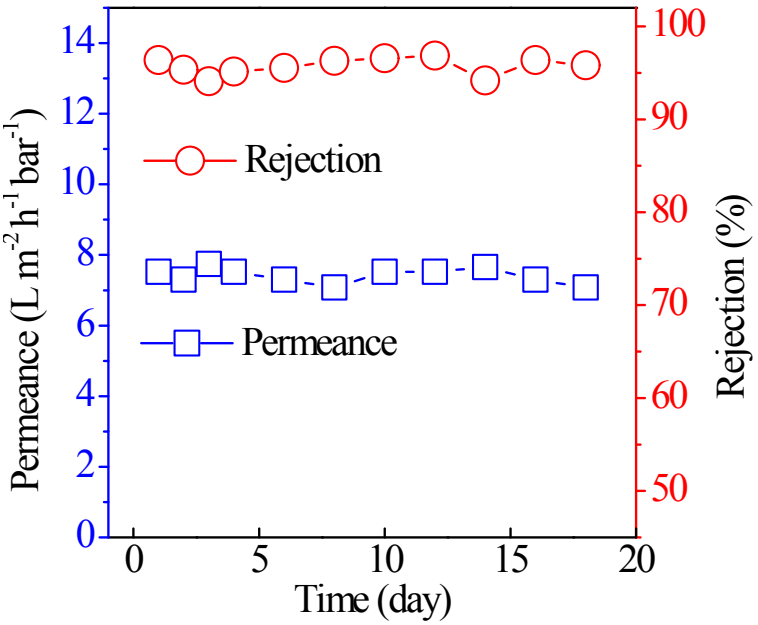

Fig. S9 Long-term desalination of the SGO-W/PES membrane at 2.0 bar. The separation performance showed small fluctuation over 18 days.