Supplementary Information

for

Nanoslitting Phase-separated Block Copolymers by Solvent Swelling for Membranes with Ultrahigh Flux and Sharp Selectivity

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Experimental Details

Membrane Preparation. Polystyrene-*b*-poly-2-vinylpyridine block copolymer (BCP, PS-*b*-P2VP, 50,000-16,500 g/mol, with a polydispersity of 1.09) was purchased from Polymer Source, Inc. (Canada), and was used as received. Chloroform (Purity > 99.8 %), ethanol (Purity > 98 %) were obtained from Sigma Aldrich and were used without further purification. A 42-nm BCP layer was prepared by spin coating a 0.5 wt % chloroform solution of PS-*b*-P2VP onto silicon wafers with 1000-nm sacrificial silicon oxide layers (4000 rpm, 30 s). The BCP-deposited silicon substrates were transferred into a 130-ml weighing bottle which served as the annealing chamber filled with approximately 6 ml TCE (1, 1, 2-trichloroethane, purity > 99.8 %, obtained from aladdin without further purification) and placed on a support extending from the surface of TCE inside the bottle. The chamber was covered with a lid immediately after placing the silicon substrates inside, allowing the annealing of the BCP films under saturated TCE vapor. After annealing for 260 s, the lid of the annealing chamber was opened and the BCP film was quickly removed from the chamber and placed in air at room temperature for at least 30 min. Then the annealed BCP film together with the silicon substrate was immersed in 5 wt % hydrofluoric (HF) solution. The BCP film was floated onto the surface after immersion for approximately of 30 s-60 s. We then collected the floating, free-standing BCP film on a polyethersulfone (PES) membrane (Tianjin Jinteng Instrument Co. Ltd) with an average diameter of 0.45 μm, producing a two-layered composite membrane. The BCP film supported on the PES membrane was subsequently treated in ethanol at 50 ºC for preset durations

followed air drying at room temperature for at least 3 h.

Characterizations. The thicknesses of BCP films were measured by a spectroscopic ellipsometer (M-2000U, J.A. Woollam. Co. Inc.) over the wavelength range from 246.1 nm to 999.8nm at a 65º incident angle. The surface topography image of the annealed BCP film was characterized by an atomic force microscope (XE-100, Park Systems). Field-emission scanning electron microscopy (Hitachi S4800) was used to view the surfaces and the cross sections of the membranes at a voltage of 5 kV. For the transmission electron microscopy (TEM) observation, the 25.6-nm-thick BCP film containing monolayer P2VP cylinders was obtained by spin-coating 0.3 wt % chloroform solution of PS-*b*-P2VP onto silicon wafers with 1000-nm silicon oxide layers (2500 rpm, 30 s). The 25.6-nm-thick BCP film was annealed and transferred onto a copper grid, and subsequently swelled in ethanol at 50 ºC for 3h followed by air drying for 24 h. TEM observation was carried out with a JEM-2100 microscope operated at 200 kV. Grazing incident small-angle X-ray scattering (GISAXS) (Nano-Viewer, Rigaku) was performed to assess the structures of the BCP films. Cu KR X-ray beams of 40 kV and 30 mA (λ = 1.54 Å) were used. The BCP films was illuminated at a grazing angle of 0.1° or 0.2° to obtain the 2D GISAXS data collected by PILATUS 100 K of 83.8×33.5 mm^2. Each X-ray exposure duration was 20 min. In-plane scan cuts were imposed on the 2D GISAXS pattern to yield the 1D profile, so the one-dimensional (1D) scattering intensity was clearly observed. BCP films spin-coated on silicon wafers were subjected to different treatments, for example, TCE annealing, ethanol swelling for different durations were analyzed by a contact

angle goniometer (DropMeter A100, Maist) and XPS (Kratos Axis Ultra DLD, Shimadzu-Kratos Co.). Contact angle measurements were performed at five different positions on each sample and the averaged value was reported. XPS analysis was utilized to characterize atomic ratios of nitrogen and carbon using a monochromatic Al Kα (1486.6 eV) X-ray source.

Water Flux and Filtration. Flux experiments were performed using a Millipore test cell (Amicon 8010, Millipore Co.) at a stirring speed of 600 rpm and a pressure of 0.1 bar under room temperature. The test cell had a working volume of 10 mL and an effective membrane area of 4.1cm^2. Before a flux test, a pre-compaction at 0.1 bar was carried out for 10 min to obtain a stable water flux. Bovine serum albumin (BSA, molecular weight 67,000 g/mol, with purity > 97 %, Sigma-Aldrich) was dissolved in phosphate buffer (pH=7.4) at a concentration of 0.5 g/L and was used to probe the retentions of the composite membranes prepared at different conditions. The BSA concentrations in feeds and filtrates were monitored using a UV-vis absorption spectrometer (NanoDrop 2000c, Thermo) and the intensities of the BSA characteristic peak at the wavelength of 280 nm of the feed and filtrate were compared to determine the retention rate of BSA of each membrane. Colloidal gold monodisperse particles (10 nm and 2 nm, BBI International) were mixed as the feed solution to assess the size-discrimination performance of the composite membrane with the BCP selective layer subjected to ethanol swelling at 50 ºC for 3 h. The feed, retentate and filtrate were measured by the UV-vis absorption spectrometer at the wavelength of 522 nm. A particle size analyzer (Nanoplus, Micromeritics) was used to measure the particle

size distribution of the feed and filtrate in the case of the refractive index of 0.47 and the absorption of 0.01. To further determine whether 2-nm-gold particles remained in the filtrate, we utilized an inductively coupled plasma emission spectrometer (PE 7000DV, PerkinElmer) to measure the concentrations of gold element in the feed and retentate.

Additional Characterization results

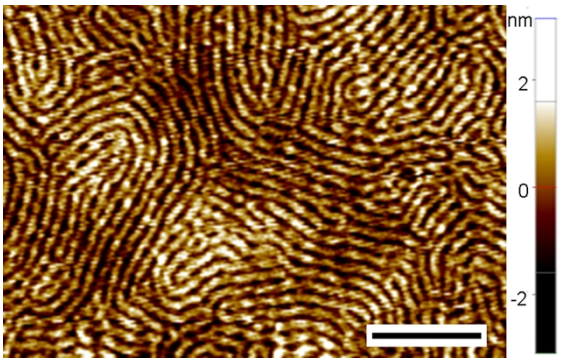

Figure S1. The AFM height image of the TCE-annealed BCP film with the P2VP cylinders parallel to the substrate surface. The scale bar is 400 nm.

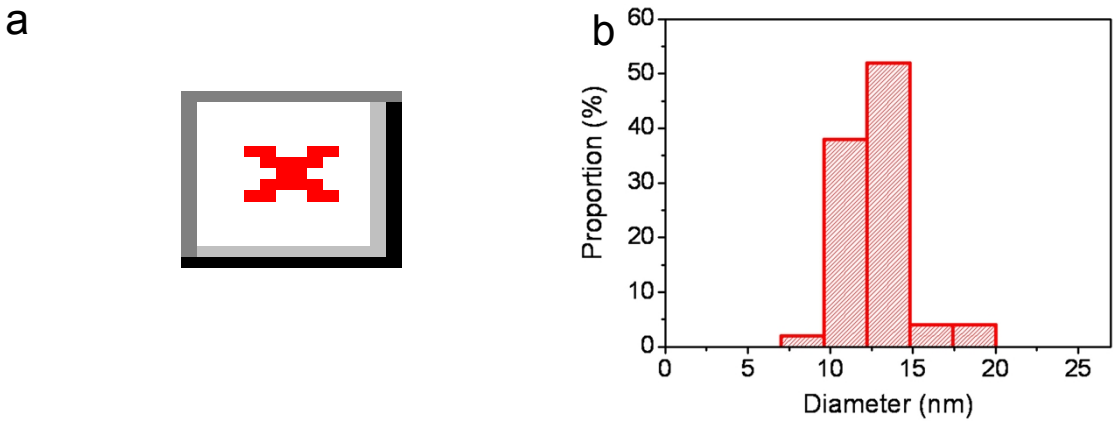

Figure S2. (a) The TEM image of the TCE-annealed BCP film subjected to ethanol swelling at 50 ºC for 3 h. The scale bar is 400 nm; (b) The pore size distribution of the

BCP film surface from the TEM image.

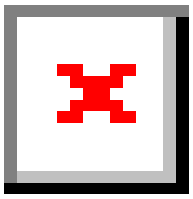

Figure S3. The 2D GISAXS pattern of the TCE-annealed BCP film subjected to ethanol swelling at 50 ºC for 3 h.

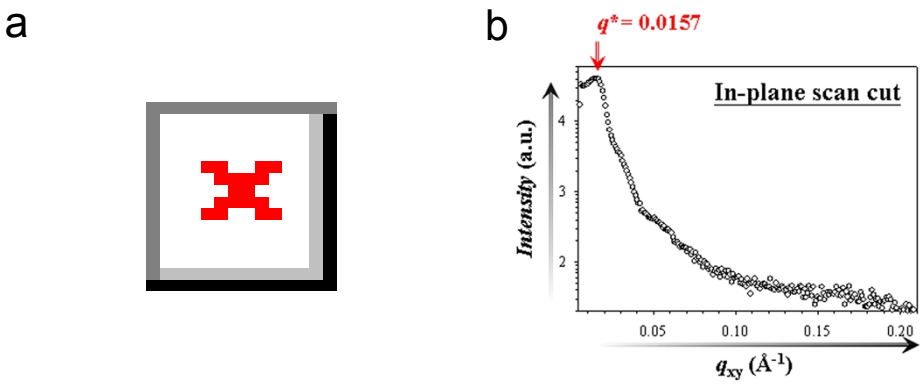

Figure S4. (a) The 2D GISAXS pattern of the as-coated film subjected to ethanol swelling at 50 ºC for 3 h; (b) The corresponding in-plane scattering profile of **a**.

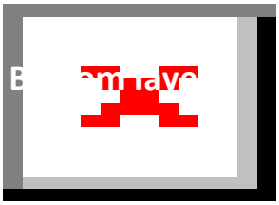

Figure S5. The surface SEM image of a BCP membrane with exposed slitted pores in the bottom layer. The scale bar corresponds to 200 nm.

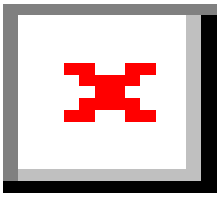

Figure S6. The SEM image of a membrane with a monolayer of slitted pores deposited on a silicon substrate which was derived from a thin BCP film with a thickness of 25.6 nm.

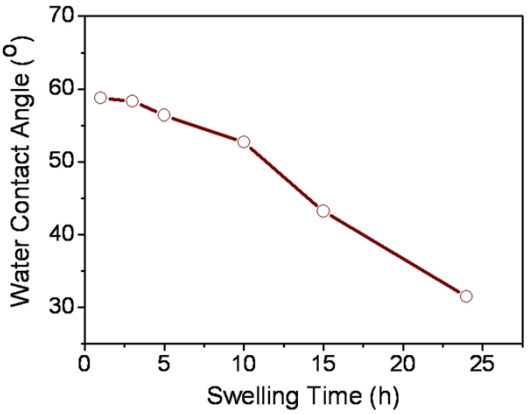

Figure S7. Water contact angles of PS-*b*-P2VP films subjected to ethanol swelling at 50 ºC for different durations.

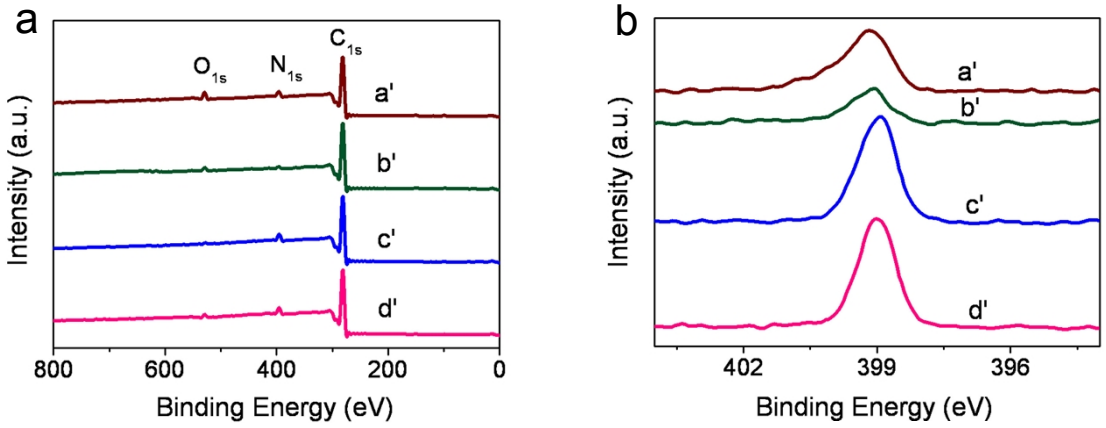

Figure S8. (a) XPS wide-spectra; (b) The corresponding enlarged spectra. XPS detailed the peak of N_{1s} of PS-*b*-P2VP films subjected to different treatments: the as-coated film subjected to ethanol swelling at 50 ºC for 3 h (a'), and the TCE-annealed film before (b') and after ethanol swelling at 50 ºC for 3 h (c') and 24 h (d').

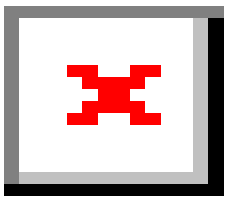

Figure S9. The surface SEM image of the as-coated BCP film with a thickness of 42 nm subjected to ethanol swelling at 50 ºC for 3 h.

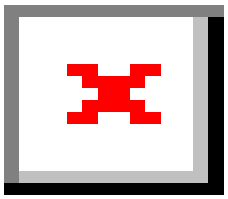

Figure S10. The surface SEM image of the BCP membrane subjected to swelling at 50 ºC for 1 h

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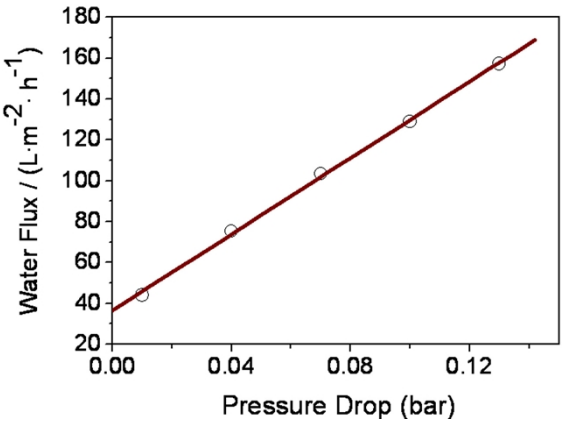

Figure S11. The fit-linear curve of flux and transmembrane pressure of the composite membrane with the BCP selective layer subjected to ethanol swelling at 50 ºC for 3 h.

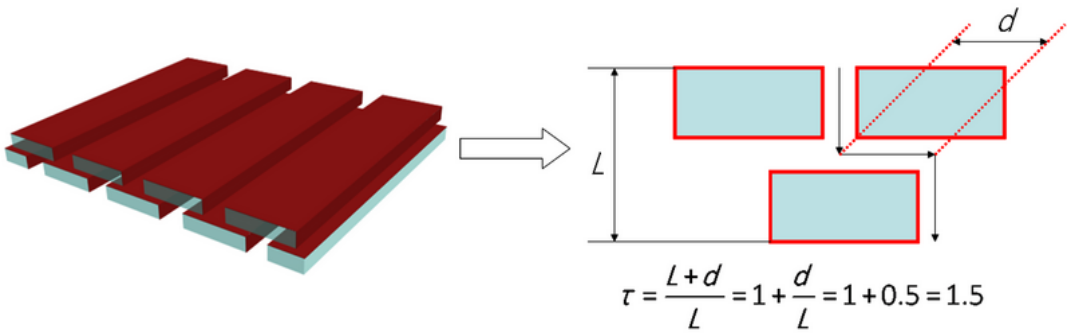

Figure S12. The value of *d* is nearly one half of the thickness of the selective layer from the analysis by SEM.

a b

Figure S13. (a) The SEM image of PES supporting membrane; (b) The corresponding binary image of **a** developed by Image J. The surface porosity of the membrane is estimated to be 0.17, based on the binary image. Scale bars are 50 μm for **a** and **b**.