Supplementary Information

for

Stretched Isoporous Composite Membranes with Elliptic Nanopores for External-Energy-Free Ultrafiltration

Leiming Guo, Lei Wang, and Yong Wang*

State Key Laboratory of Materials-Oriented Chemical Engineering, National Engineering Research Center for Specialized Membranes, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, Jiangsu, China

*Corresponding authors.

E-mail: yongwang@njtech.edu.cn

Tel: 0086-25-8317 2247

Fax: 0086-25-8317 2292
**Experimental Details**

**Membrane Preparation.** Polystyrene-\(b\)-poly-2-vinylpyridine block copolymer (BCP, PS-\(b\)-P2VP, 290,000-72,000 g/mol, with a polydispersity of 1.10) and PS-OH (6,000 g/mol, PDI=1.07) were purchased from Polymer Source, Inc. (Canada), and were used as received. Chloroform (Purity > 99.8 %), ethanol (Purity > 98 %) were obtained from Sigma Aldrich and were used without further purification. According to our previous work,\(^{[15]}\) a 70-nm BCP layer was prepared by spin coating a 0.6 wt % chloroform solution of PS-\(b\)-P2VP onto the PS-OH-grafted silicon wafers with 1000-nm sacrificial silicon oxide layers (2000 rpm, 30 s), producing the BCP films. Subsequently, the BCP film was annealed under the saturated vapor of chloroform in a home-built chamber. Then the BCP film was floated onto the surface of 5 wt % hydrofluoric (HF) solution and transferred onto a polyethersulfone (PES) membrane (Tianjin Jinteng Instrument Co. Ltd) with an average diameter of 0.22 \(\mu\)m, producing a bilayered composite membrane. The BCP film supported on the PES membrane was subsequently treated in ethanol at 60 \(^\circ\)C for 10 h followed by air drying at room temperature for at least 3 h. The mechanical stretching of composite membranes were carried out on an electronic tensile tester (CMT-6203, Shenzhen Sans Test Machine Co.) with a tensile rate of 2 mm/min. The samples were prepared in the dimension of 2.0 \(\times\) 2.0 cm\(^2\) and fixed to be stretched with the elongation of 20%, 40%, and 60%, respectively.
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 999.8 nm at a 65° incident angle. Field-emission scanning electron microscopy (Hitachi S4800) was used to probe the surfaces and the cross sections of the membranes at a voltage of 5 kV.

Water Flux and Filtration. Gravity-driven filtration was performed on a homemade filtration set (Figure S4) at room temperature. This setup had a working volume of 25 mL (the residual 2.5 mL is neglected in the filtration process) and an effective membrane area of $1.0 \times 1.0 \text{ cm}^2$ was used. The water flux is calculated by the equation of $J = \frac{\Delta V}{s \cdot t}$ ($\Delta V = 5 \text{ mL}$; $s$ is the effect area of membranes and determined as $1.0 \text{ cm}^2$; $t$ is the recorded time that water penetrates every 5 mL). 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 stretched 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. 30 nm colloidal monodispersed gold particle solution (BBI International) was further utilized as the rejection solute. Before filtration, membranes were conditioned with Acid Orange 7. Briefly, 5 mg/L Acid Orange 7 (> 85%,
$M_w=350.32$ Da, Aladdin) was permitted to penetrate through membranes for 30 min followed by water washing and air-drying. The feed and filtrate were measured by an inductively coupled plasma emission spectrometer (PE 7000DV, PerkinElmer) for the filtration of 30 nm nanoparticles. Colloidal gold monodispersed particles (30 nm and 10 nm, BBI International) were mixed as the feed solution to assess the size-discrimination performance of the composite membrane with 20% strain. The feed and filtrate were measured by a particle size analyzer (Nanoplus, Micromeritics). To further determine whether 10-nm-gold particles remained in the filtrate, we utilized the inductively coupled plasma emission spectrometer to measure the concentrations of gold element in the feed and filtrate.
**Figure S1.** The SEM images (a, c, e, g) and the corresponding binary images (b, d, f, h) generated by the software of *Image J* of the PES support membranes with 0% (a, b), 20% (c, d), 40% (e, f) and 60% (g, h) strains, respectively. The surface porosities of the stretched PES membranes are estimated to be 0.102, 0.132, 0.143 and 0.142, respectively, based on the binary images. All the images have the same magnifications and the scale bar is shown in (a).
The surface porosities of the stretched membranes.

The surface porosity of the circular pores is estimated by the equation

\[ \varepsilon = \frac{n_p \pi r^2}{A_m} \]  

(1)

where \( \varepsilon \) is the surface porosity, \( n_p \) is the number of pores, \( r \) is the pore radius and \( A_m \) is the total membrane area. The porosity of the cylindrical pores is thus calculated to be 11.7 %.

For stretched membranes, we assume that the pore shapes of the BCP layers on the areas of micropores of the PES are elliptical, the effective porosities of the BCP layers are estimated by the equation

\[ \varepsilon = \frac{n_p \pi \alpha \beta}{A_m} \]  

(2)

where \( \varepsilon \) is the surface porosity, \( n_p \) is the number of pores, \( \alpha \) is the half pore length, \( \beta \) is the half pore width and \( A_m \) is the total membrane area. The effective porosities of the stretched membranes are calculated as 14 %, 17.5 %, and 19.9 % with the elongations of 20%, 40% and 60%, respectively. It should be noted that the effective porosities indicate the areas that water could pass through.
Figure S3. The picture of setup for the gravity-driven ultrafiltration used in this work.
Figure S4. The histograms of the filtration times of the composite membranes with different strains vs the volume changes of water columns in the filtration setup.

S5. The calculation of water pressure

The linear distances of the positions of 25 mL and 20 mL to the composite membrane are 11 cm and 9 cm, respectively. Therefore, the average water pressure is roughly estimated as following:

\[ P = \frac{1}{2} \int_{9}^{11} PdP = 0.01bar \] (3)
Figure S6. The size-distribution curve of gold nanoparticles with the diameter of 30 nm.
Figure S7. The photographs (a, c, e) and the corresponding SEM surface images (b, d, f) of the composite membrane with 40% strain. The stretched membrane after filtration with gold nanoparticles (a, b), the stretched membrane was conditioned in Acid Orange 7 for 30 min (c, d), and the conditioned membrane after filtration with gold nanoparticles (e, f).
Table S1. The structural parameters of the composite membranes with different strains.

<table>
<thead>
<tr>
<th>Strain (%)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J/ L/ (\text{bar} \cdot \text{m}^2 \cdot \text{h})$</td>
<td>2040</td>
<td>8570</td>
<td>13040</td>
<td>15000</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>11.7%</td>
<td>14%</td>
<td>17.5</td>
<td>19.9</td>
</tr>
<tr>
<td>$\delta_m/ \text{nm}^a$</td>
<td>85</td>
<td>70.8</td>
<td>60.7</td>
<td>53</td>
</tr>
<tr>
<td>$\varepsilon'$</td>
<td>10.2%</td>
<td>13.2%</td>
<td>14.3%</td>
<td>14.2%</td>
</tr>
<tr>
<td>Pore Length/ nm</td>
<td>35</td>
<td>89.6</td>
<td>117</td>
<td>134.3</td>
</tr>
<tr>
<td>Pore Width/ nm</td>
<td>35</td>
<td>37</td>
<td>48.6</td>
<td>48.2</td>
</tr>
</tbody>
</table>

$^a$ The thicknesses of the stretched BCP layers are roughly calculated by $\delta_m=V/(a \times b)$, where $a \times b$ is the area of the BCP layer. We assumed the elongation occurred along $b$ direction, then it has a relationship of $\delta_m \propto b$. 