Supplementary Materials (ESI) for *Journal of Materials Chemistry*

Supplementary Information:

Ultrathin free-standing nanoporous membranes prepared from polystyrene nanoparticles

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1. Nanofibrous sacrificial layer

Nanofibrous sacrificial layer was prepared by filtering an aqueous dispersion of cadmium hydroxide nanostrands (10 mL) on a polycarbonate (PC) membrane (pore size: 0.2 μm, filter area: 2.84 cm^2) at 80 kPa. This porous nanofibrous layer with a thickness of ~150 nm has a high permeability for water, but nanoparticles larger than 10 nm cannot pass the pores.

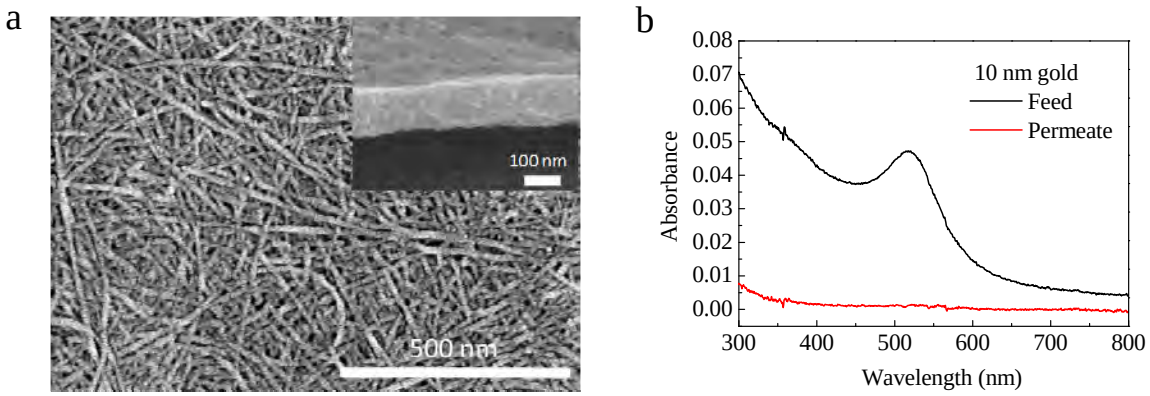

Figure S1 (a) Top and cross-sectional SEM images of nanofibrous sacrificial layer made of cadmium hydroxide nanostrands. (b) UV-vis absorption spectra of feed and permeate solutions of 10 nm gold nanoparticles.

The SEM images and rejection performance for gold nanoparticles are shown in Figure S1. When an aqueous solution of 10 nm gold nanoparticles was filtered on a nanofibrous sacrificial layer, the absorbance near 520 nm, which is due to the plasmon resonance of gold nanoparticles, completely disappeared in the permeate. The average flux of water was about 5000 $L \cdot m^{-2} \cdot h^{-1}$ at pressure difference of 80 kPa.

2. Filtration of PS nanoparticles

Figure S2 shows SEM images of 50 nm PS nanoparticles filtered on a nanofibrous sacrificial layer of cadmium hydroxide nanostrands. The filtration was performed with 1 mL of the nanoparticle solution in ethanol (10 μg·mL^{-1}) at the conditions described in our article. As shown in the top view, PS nanoparticle layer was not very uniform and several big pores existed in the layer (however, these big pores could be completely filled after repeating filtration and cross-linking procedures). From the cross-sectional view, it is clear that pores of PC membrane are covered with a 150-nm-thick sacrificial layer of cadmium hydroxide nanostrands and a PS nanoparticle layer locates on the sacrificial layer.

Filtration time of 15 nm, 25 nm, and 50 nm PS nanoparticle solutions was 2 min, 1 min, and 20 sec, respectively. The second filtration of these nanoparticle solutions took about 3 min because of the existence of pre-formed nanoparticle layers.

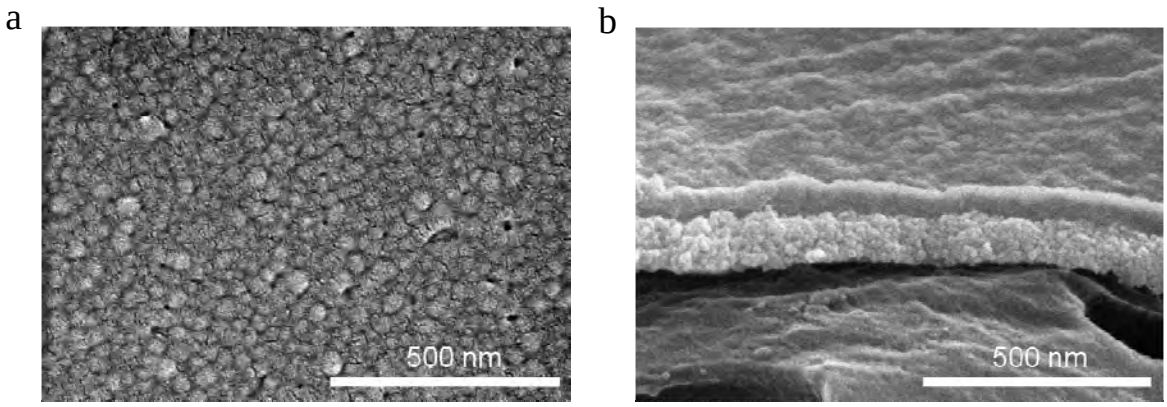

Figure S2 (a) Top and (b) cross-sectional SEM images of 50 nm PS nanoparticles assembled on a nanofibrous sacrificial layer.

3. Preparation of PS nanoparticle layer on a substrate with micron pores

10 mL aqueous solution of copper hydroxide nanostrands was filtered on a cellulose acetate membrane (cut off of 0.2 μm, *Advantec*) by suction filtration at 80 kPa, then 2 mL of 50 nm PS nanoparticle solution (10 μg·mL^{-1}) was filtered. Procedures of copper hydroxide nanostrands are similar to those of cadmium hydroxide nanostrands. An aqueous solution of 1.0 mM 2-aminoethanol was quickly mixed with an equivolume of 4 mM copper nitrate and allowed to stand for 7 days at 15 ^{o}C to form copper hydroxide nanostrands.

Figure S3-a shows a top-view image of cellulose acetate membrane. The surface was not smooth, and the pore size was appeared to be more than 2 μm at the membrane surface. 10 mL aqueous solution of copper hydroxide nanostrands could form a uniform layer with a

thickness of ~150 nm on the membrane, as shown in Figure S3-b and S3-c. Furthermore, 50 nm PS nanoparticle layer formed the homogeneous layer with a thickness of ~80 nm on the copper hydroxide nanostrand layer by suction filtration (Figure S3-d).

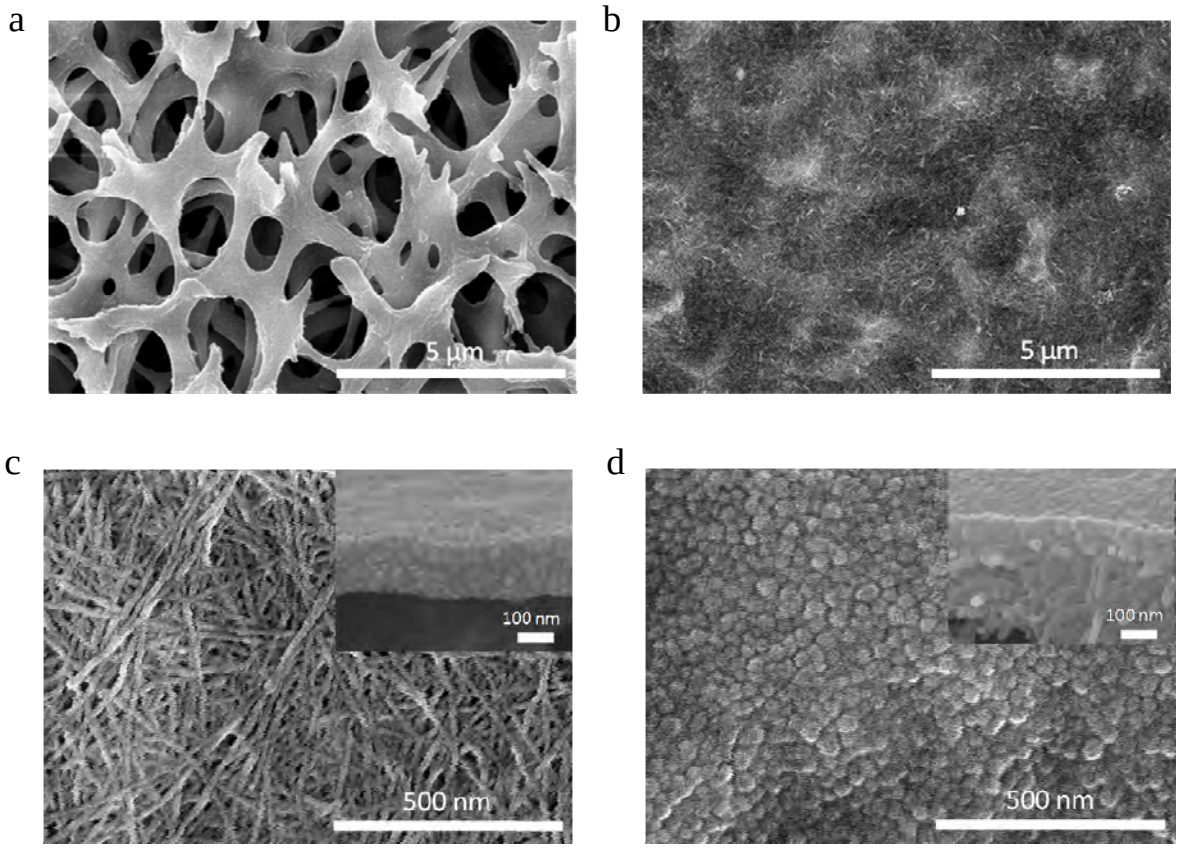

Figure S3 (a) Top-view SEM image of cellulose acetate membrane. (b) and (c) SEM images of copper hydroxide nanostrand layer filtered on the cellulose acetate membrane. (d) SEM images of 50 nm PS nanoparticle layer prepared on the copper hydroxide nanostrand layer.

4. Separation of Cyt.c using cross-linked 15 nm PS nanoparticle membranes

Figure S4 shows UV-vis absorption spectra of Cyt.c solutions separated by cross-linked 15 nm PS nanoparticle membranes at pH 7 and 12. Separation at pH 2.34 is shown in Figure 3-a of our article. The spectra were obtained after one-fourth of the solutions were filtered. The permeate did not contain Cyt.c. The cross-linked PS nanoparticle membranes were stable at least in a pH range of pH 2 – 12.

Adsorption of Cyt.c on the surface of the membrane was more significant at neutral and alkaline conditions than acidic condition. At pH 2.34, the concentration in the upper stream

increased more than 35%, and the rejection was 94% from the increase in the upper stream. This means that 6% Cyt.c adsorbed on the membrane surface. At pH 12, the rejection was 77.2% from the increase in the upper stream, then 22.8% Cyt.c adsorbed on the membrane surface. And at pH 7, the concentration in the upper stream is less than that in the feed. Therefore, we concluded that the experiments at neutral and alkaline conditions include the effect of electrostatic adsorption of the protein on cross-linked PS nanoparticle membranes.

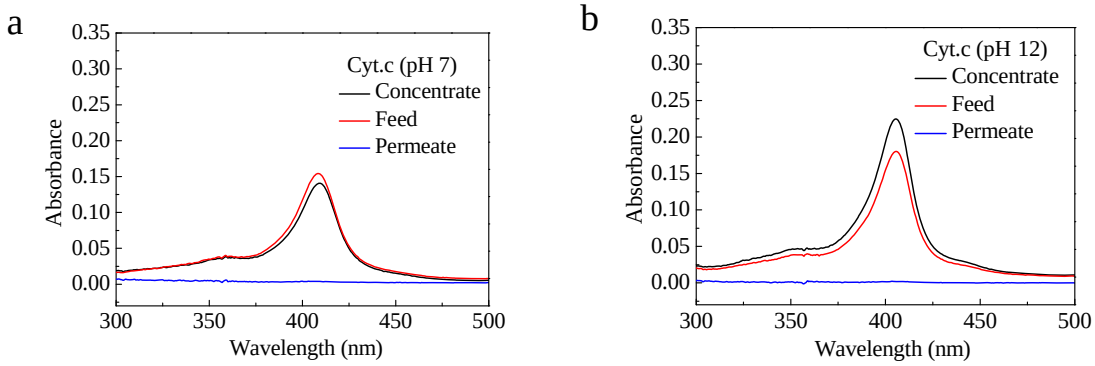

Figure S4 UV-vis absorption spectra of Cyt.c solutions concentrated by and permeated through 15 nm PS nanoparticle membranes. Cyt.c solutions: pH 7 (a) and 12 (b).

5. Nanoporous membranes prepared from 25 nm PS nanoparticles

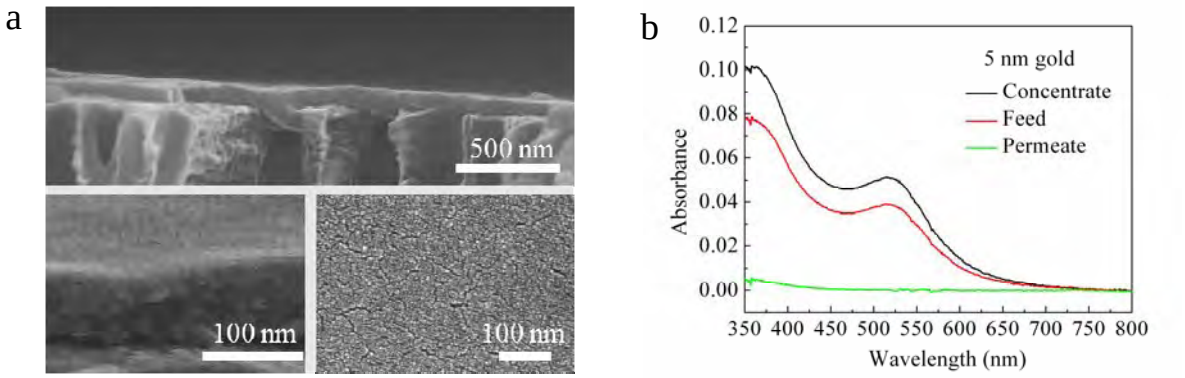

Figure S5. (a) SEM images of ultrathin cross-linked 25 nm PS nanoparticle membranes prepared and (b) UV-vis absorption spectra of 5 nm gold nanoparticle solutions concentrated by and permeated through the PS nanoparticle membrane.

Figure S5 shows SEM images of cross-linked 25 nm PS nanoparticle membranes and the filtration performance. The membranes were prepared similarly to those of 50 nm (or 15 nm) PS nanoparticle membranes. The images were obtained after depositing a 2-nm-thick Pt layer on the specimens. The thickness was estimated to be ~80 nm from the cross-sectional views.

Cracks on the surface of the membrane were formed by electron beam irradiation during SEM observation. This membrane had pores of about 4 nm and completely rejected 5 nm gold nanoparticles at pH 7.0. When one-third volume of the nanoparticle solution was filtered, the concentration in the upper stream increased, as shown in Figure S5-b. The rejection calculated from the permeate was 100%, while the rejection calculated from the upper stream concentration increased from the feed was 66.5%.

6. Filtration performance of defective PS nanoparticle membranes

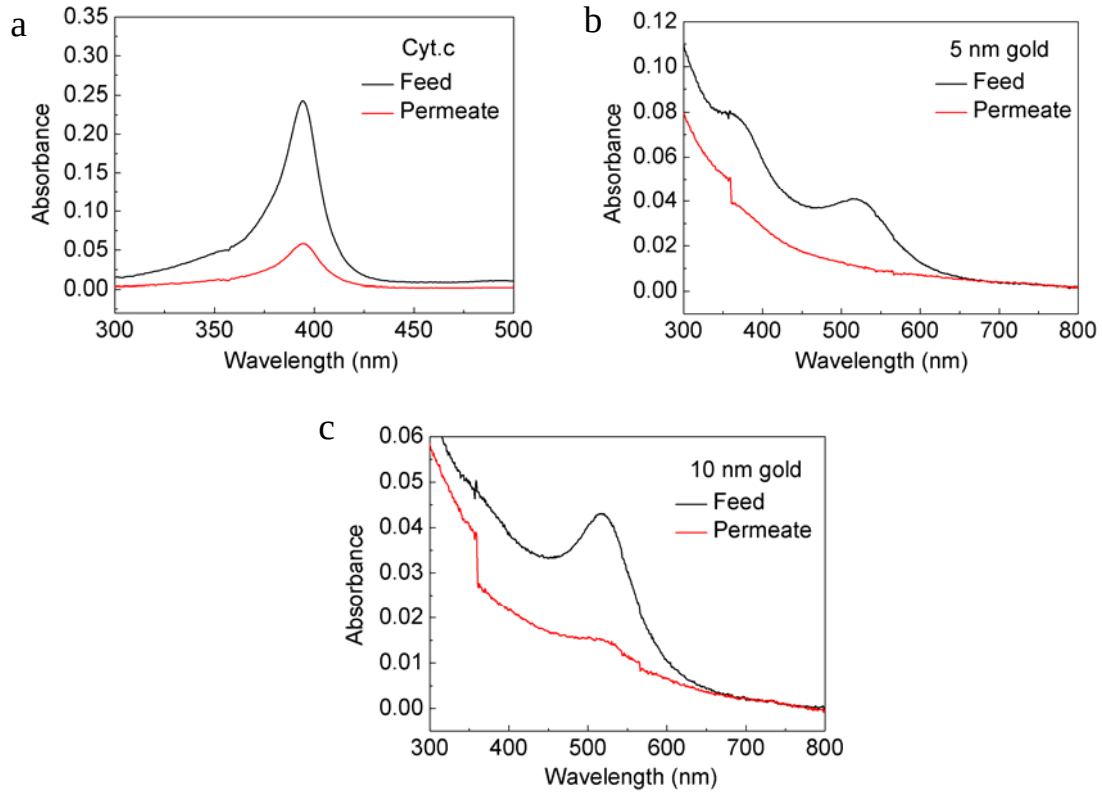

Figure S6 Changes of UV-vis absorption spectra before and after filtering with a "defective" PS nanoparticle membrane. (a) Cyt.c solution at pH 2.34 was filtered with the membrane made of 15 nm PS nanoparticles. (b) 5 nm gold nanoparticle solution at pH 7.0 was filtered with the membrane made of 25 nm PS nanoparticles. (c) 10 nm gold nanoparticle solution at pH 7.0 was filtered with the membrane made of 50 nm PS nanoparticles.

Figure S6 shows the changes in UV-vis absorption spectra of Cyt.c, 5 nm gold nanoparticle, and 10 nm gold nanoparticle solutions before and after filtering with an ultrathin cross-linked PS nanoparticle membrane. In our article, we explained that perfect rejection was achieved for the membranes prepared by repeating filtration and cross-linking procedures twice. For the

comparison, we prepared the reference membranes by filtering a given volume of PS nanoparticle solution at one time. The resultant membranes had many big pores (see Figure S2) and these pores significantly decreased the rejection performance, as shown in Figure S6. For example, the membrane prepared by single filtration and cross-linking process of 15 nm PS nanoparticles gave 77.1% rejection for Cyt.c (Figure S6-a). Similarly, 25 nm and 50 nm PS nanoparticle membranes prepared by single filtration and cross-linking process showed 72.6% and 64.3% rejection for 5 nm gold nanoparticles and 10 nm gold nanoparticles, respectively (Figure S6-b and S6-c). These membranes have perfect rejection, if prepared by repeating filtration and cross-linking procedures twice.

7. Separation of Cyt.c using commercial membranes

To compare filtration performance of cross-linked PS nanoparticle membranes and that of commercial membranes, we measured pure water flux and rejection of Cyt.c through *Ultracel PL* membranes (*Millipore*) with a cut-off of 5 k (membrane code: *PLCC*) and 10 k (membrane code: *PLGC*). These commercial membranes can be performed in a pH range of 3 – 13. As suction filtered at pH 3.12 and at the pressure difference of 80 kPa in our experimental set up, *PLCC* membrane had pure water flux of 5.6 $L \cdot m^{-2} \cdot h^{-1}$ and completely rejected Cyt.c. *PLGC* membrane had pure water flux of 22.1 $L \cdot m^{-2} \cdot h^{-1}$ and the rejection of Cyt.c was 70.5 %. Compared to *PLCC* membrane, the cross-linked 15 nm PS nanoparticle membrane had 34-times larger flux for pure water, giving perfect rejection for Cyt.c. And compared to *PLGC* membrane, the nanoparticle membrane had 8.6-times larger pure water flux.

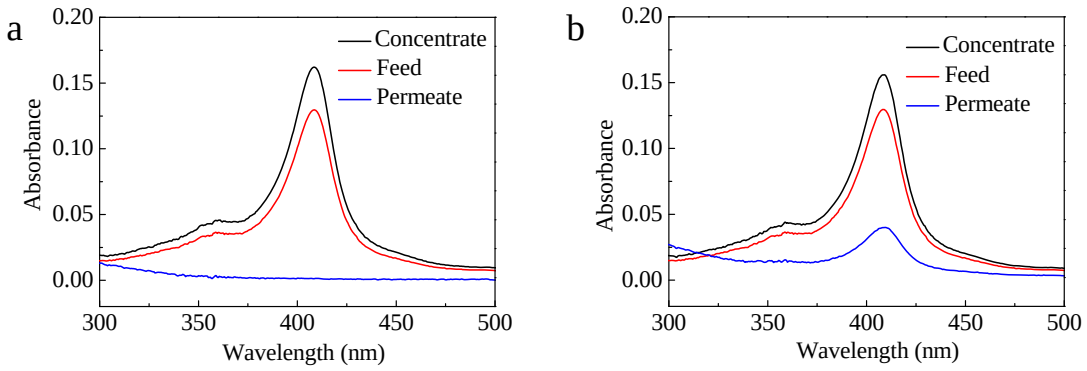

Figure S7 UV-vis absorption spectra of Cyt.c solutions concentrated by and permeated at pH 3.12 through *Ultracel PL* membrane with a cut-off of 5k (a) and 10k (b).