Supporting Information for Nanoscale

Ultrathin self-assembled anionic polymer membranes for superfast size-selective separation

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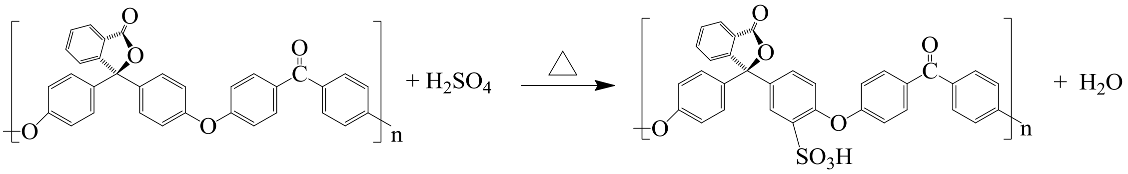
1. Synthesis and characterization of SPEK-C

10 g of PEK-C was dissolved in concentrated sulfuric acid (180 ml) for 40 min, and the reaction between PEK-C and sulfuric acid occurred simultaneously. The reaction proceeded in the homogeneous solution at 40 °C for a desired time (varying from 1 to 30 h) to obtain SPEK-C (H) with various *SD*s. The reaction is shown in Scheme S1. The SPEK-C (H) solution was quenched in deionized water under mechanical stirring. The precipitant was then repeatedly washed using deionized water to remove the residual sulfuric acid until the pH of the washing water in equilibrium with the SPEK-C (H) precipitate was in between 6 and 7.



Scheme S1. Synthesis of SPEK-C (H) by reaction of PEK-C and sulfuric acid.

The *SD* of SPEK-C (H) was determined by titration method. 1 g of SPEK-C (H) was immersed in 1 M aqueous sodium hydroxide solution for 48 h. 1 M dilute hydrochloric acid was used to back-titrate the aqueous sodium hydroxide using phenolphthalein as an indicator. Ion exchange capacity (*IEC*) and sulfonation degree (*SD*) are calculated by

$$IEC = \frac{V_{NaOH} \times C_{NaOH} - V_{HCl} \times C_{HCl}}{m} \tag{S1}$$

$$SD = \frac{496 \times IEC}{1000 - 102 \times IEC} \tag{S2}$$

where *m* denotes the mass of SPEK-C (H), V_{NaOH}, V_{HCl} are the volume of aqueous sodium hydroxide and dilute hydrochloric acid, respectively. C_{NaOH} and C_{HCl} are the molar concentration of aqueous sodium hydroxide and dilute hydrochloric acid, respectively.

We prepared five kinds of SPEK-C (H) by varying the reaction time. Their *IEC* and *SD* increase with the reaction time, as shown in Figure S1. The *SD* of 0.24, 0.39, 0.58, 0.71 and 0.83 at the reaction time of 2, 4, 8, 16 and 26 h is achieved respectively.

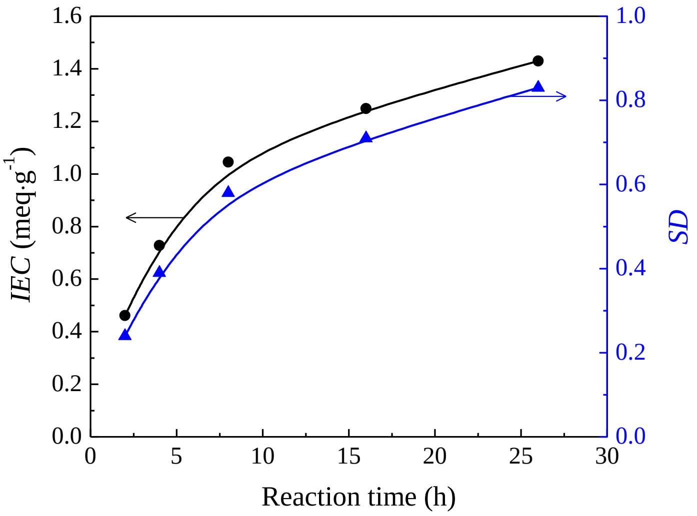


Figure S1. Effect of the reaction time on *IEC* and *SD* of SPEK-C (H).

SPEK-C (H) with -SO_3H groups will dissolve copper hydroxide nanostrands in preparing membranes. Thus, the SPEK-C (H) was immersed in 1 M aqueous sodium hydroxide solution for 48 h, and then repeatedly washed using deionized water to remove the residual sodium hydroxide. After being dried, the SPEK-C with -SO_3Na groups was obtained and used to prepare ultrathin self-assembled SPEK-C membranes.

2. Effect of the sulfonation degree on membrane formation

8 ml of nanostrand solution was filtered across a PTFE membrane with filtration area of 2.27 cm^2 resulting in a nanostrand layer. Then, a 0.1 $mg\cdot ml^{-1}$ SPEK-C solution with various *SD*s meandered through the nanostrand layer. After that, 10 ml of 10 mM hydrochloric acid was filtered to remove the nanostrands. The resulting SPEK-C membranes with the *SD* of

0.58 and 0.71 are shown in Figure S2. It is clear that the membrane is not formed for SPEK-C with the *SD* of 0.58, and the membrane with few defects is formed for SPEK-C with the *SD* of 0.71.

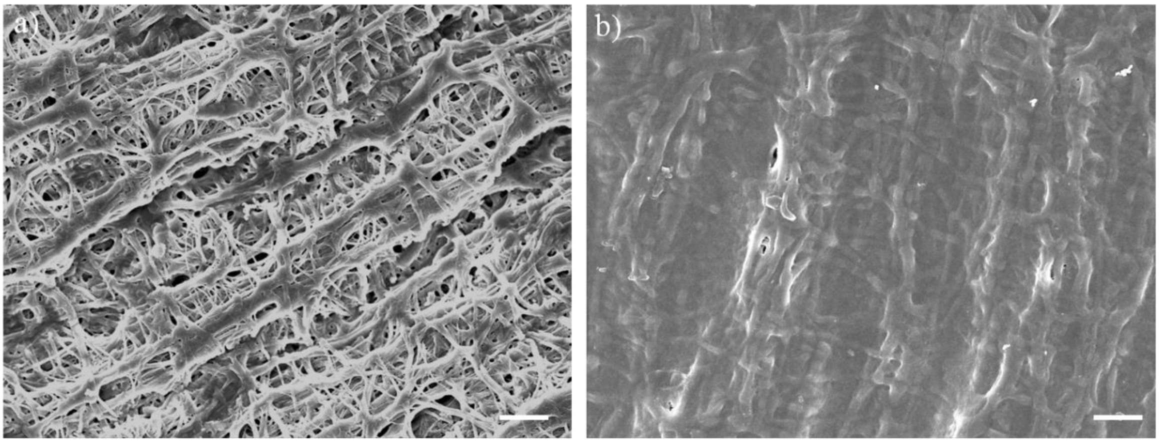


Figure S2. Top-view SEM images of self-assembled membranes prepared from SPEK-C with the *SD* of 0.58 (a) and 0.71 (b). A nanostrand layer was prepared from 3.52 ml·cm^{-2} of nanostrand solution. The scale bar is 1 μm.

3. Structure and properties of the self-assembled membranes

Table S1 lists properties of the self-assembled membranes. The membrane thickness was adjusted by filtering different volumes of nanostrand solution. The volume of nanostrand solution is in the range of 4–12 ml at the interval of 2 ml, i.e. 1.76, 2.64, 3.52, 4.41 and 5.29 ml·cm^{-2} (per cm^{2} filter area) in Table S1. The membrane thickness is estimated from the cross-sectional SEM images (Figure S3), as listed in Table S1. Water flux was measured by filtering 100 ml of deionized water across the membrane with the filtration area of 2.27 cm^{2} in a dead-end mode at suction vacuum pressure of 80 kPa. It is found to decrease with increasing membrane thickness. To investigate protein rejection, permeation of a half of the feed (8ml of protein solution) across the membrane was done. The pH of protein solutions is around neutral, which is higher than the pI of BSA and ferritin and less than the pI of cyt.c. Therefore, cyt.c molecules would be adsorbed on/in the membrane. This is why the rejection of cyt.c is more than that of BSA.

Table S1. Separation properties of the self-assembled membranes.

No.	Volume of nanostrands solution (ml·cm^{-2})	Membrane thickness (nm)	Pure water flux (l·m^{-2}·h^{-1}·bar^{-1})	Rejection (%)		
				Cyt.c	BSA	Ferritin
M-1	1.76	85 ± 12	3306	93	14.6	95.5
M-2	2.64	143 ± 16	2479	94.1	34.9	95.3
M-3	3.52	186 ± 15	2110	93.8	50.1	95.8
M-4	4.41	286 ± 18	1710	95.6	79.8	96.6
M-5	5.29	414 ± 25	1417	96.7	91.1	97.4

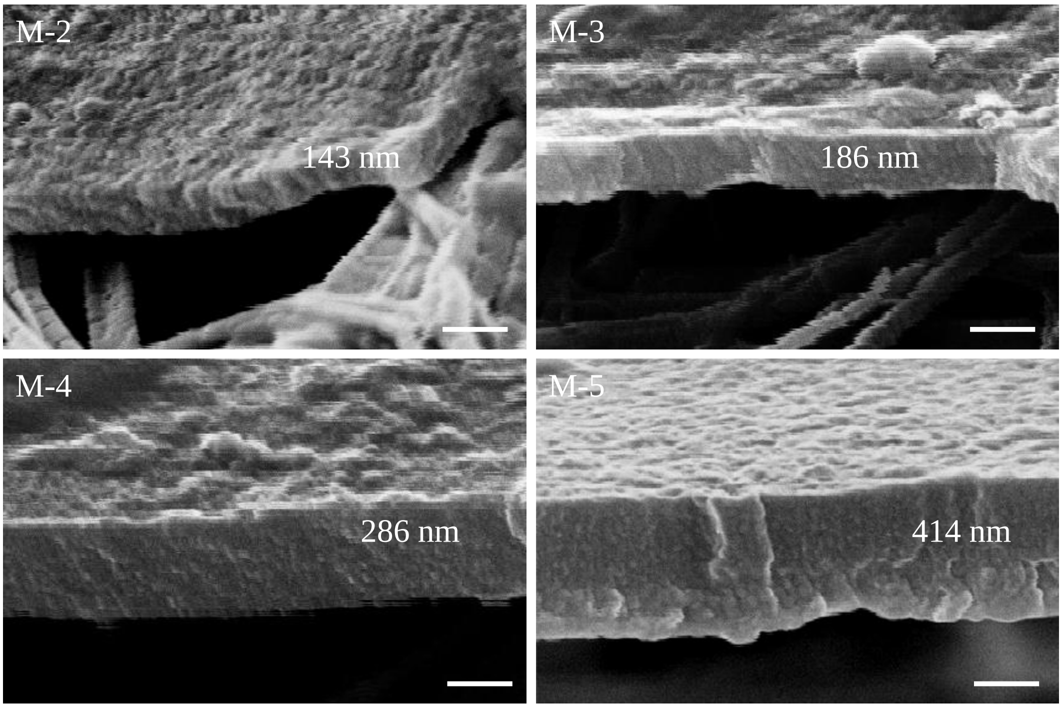


Figure S3. Cross-sectional SEM images of self-assembled membranes with different thicknesses. The scale bar is 200 nm.

Figure S4 show the rejection properties of 5 nm gold nanoparticle solution separated by the 414-nm-thick membrane. In the filtration, the feed is 8 ml and the permeate 3.64 ml, the rejection of 92.5 and 41.1 % is thus calculated from the permeate and the concentrate respectively.

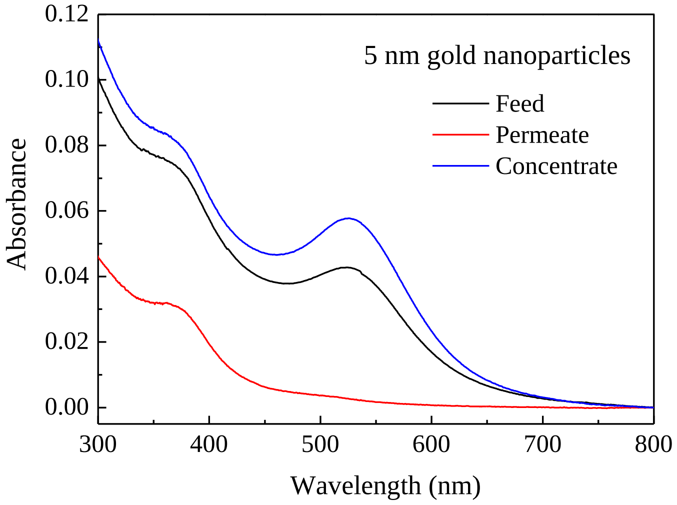


Figure S4. UV-vis spectra of the feed, permeate and concentrate for 5 nm gold nanoparticle solution separated by the 414-nm-thick self-assembled membrane.

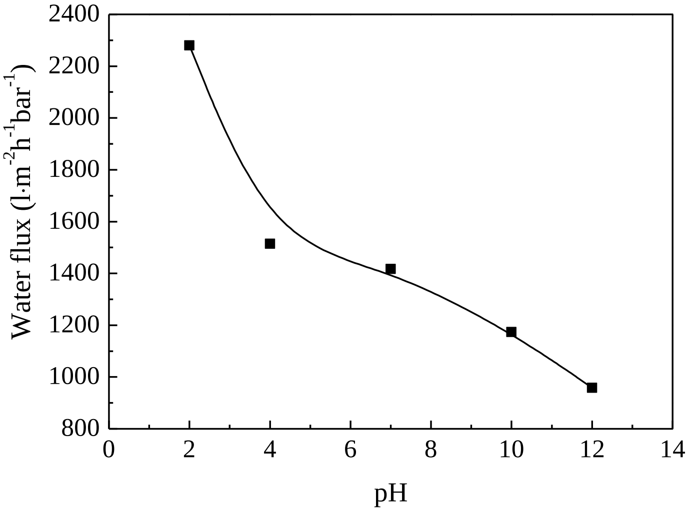


Figure S5. The pH dependence of water flux of the 414-nm-thick self-assembled membrane.

The pH dependence of water flux of the membranes was studied by filtering 40 ml of deionized water across the 414-nm-thick membrane, as shown in Figure S5. It is clear that the water flux remarkably decreases with increasing pH due to the increase in degree of ionization of SPEK-C. As a result, pores in the membrane would be smaller with increasing pH, resulting in an increase of rejection due to the size exclusive effect.

4. Cyt.c separation using the self-assembled membranes

To study effects of protein adsorption on the membrane performance, permeation of about a half of cyt.c (pI of 10.6) solution (8 ml) across the 414-nm-thick membrane was done. As shown in Figure S6, the cyt.c concentration in the concentrate is less than that in the feed when the feed pH is above the pI of cyt.c. In this case, the rejections of 98.9 and 82.0 % are artificial. However, the rejection of 9.5% is reliable for the feed with pH of 11.45.

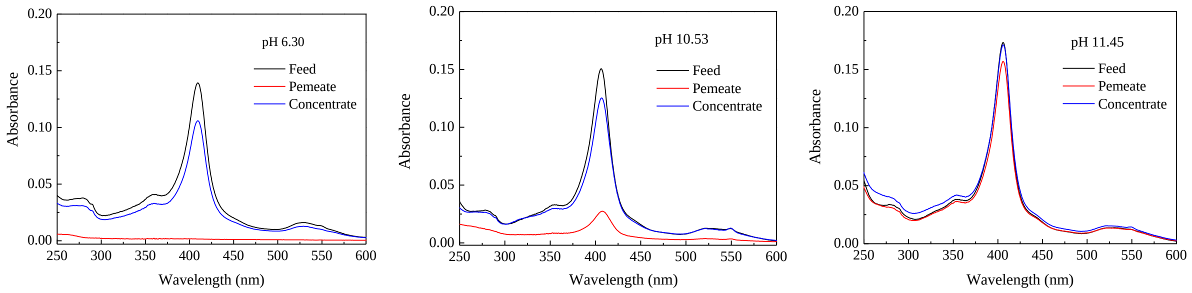


Figure S6. UV-vis spectra of the feed, permeate and concentrate for cyt.c solution separated by the 414-nm-thick self-assembled membrane.

To investigate the adsorption of cyt.c on/in the membrane, 40 ml of cyt.c solution with pH of 6.30 was filtered across the membrane. The cyt.c concentration in the permeate increases with the volume of the permeate, and reaches a constant when the permeate is more than 32 ml, as shown in Figure S7. That is, the rejection calculated from the permeate first decreases and reaches the constant minimum of ~39% that is higher than 9.5% (pH of 11.45). This suggests that the cyt.c adsorption is completed after 32 ml of feed permeated resulting in a decrease in the pore size.

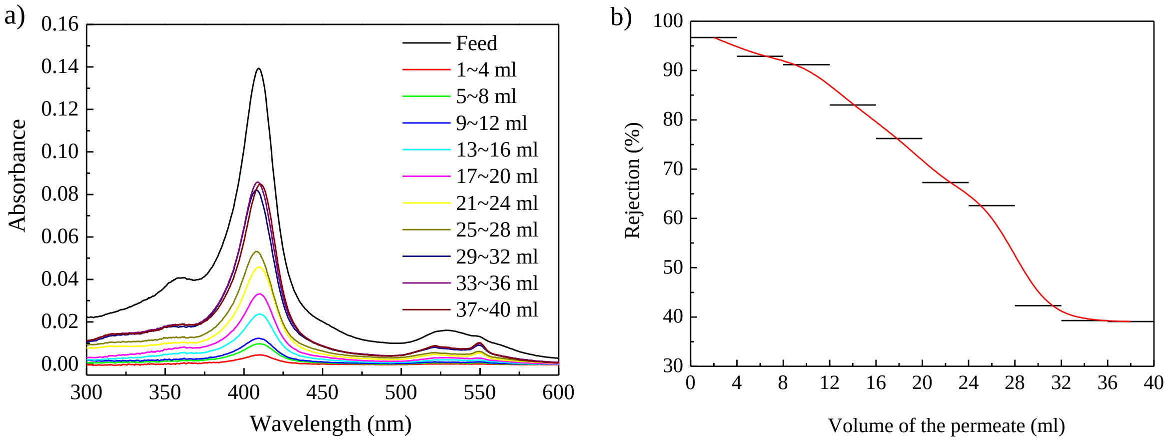


Figure S7. a) UV-vis spectra of the feed and the permeate for cyt.c solution separated by the 414-nm-thick self-assembled membrane. b) The rejection is calculated from the permeate.

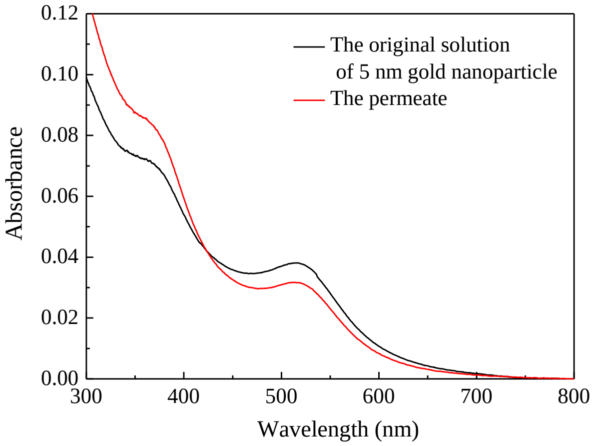


Figure S8. UV-vis spectra of the original solution of 5 nm gold nanoparticles and the permeate of the gold nanoparticle mixtures.

5. Size-selective separation of gold nanoparticles using the self-assembled membranes

To investigate the size-selective separation efficiency, we compare UV-vis spectra of the permeate and the 5 nm gold nanoparticle solution with the concentration in the feed (the mixture of 5 and 15 nm gold nanoparticles), as shown in Figure S8. It is found that 83.0 % of 5 nm gold nanoparticle was separated from its mixture.

6. Comparison with the commercial flat sheet ultrafiltration membranes

The 85-nm-thick self-assembled membrane has a ferritin rejection (12 nm in diameter) of 95.5% and a cut-off of less than 12 nm. Compared with the commercial membranes with a cut-off of 100 kDa, this membrane have ultrahigh water flux of 3306 $l \cdot m^{-2} h^{-1} bar^{-1}$ that is an order of magnitude larger than that of most commercial membranes. On the other hand, the 414 nm-thick membrane has rejection of 92.5% for 5 nm gold nanoparticles, suggesting below 5 nm cut-off. This membrane also has high water flux of 1417 $l \cdot m^{-2} h^{-1} bar^{-1}$ that is much greater than that of most commercial membranes with cut-off of 50 kDa.

Table S2. Water fluxes of the typical commercial flat sheet ultrafiltration membranes.

Designation [a]	Manufacturer	Polymer	Pore size (MWCO)	Water flux ($l \cdot m^{-2} h^{-1} bar^{-1}$)
Biomax 100	Millipore	Polyethersulfone	50 k	688.9
HFM-100	Koch	PVDF	50 k	147.9
HFM-116	Koch	PVDF	50 k	221.9
EW	GE Osmonics	Polysulfone	60 k	295.8
MW	GE Osmonics	Ultrafilic	100 k	217.0
UE50	TriSep	Polyethersulfone	100 k	123.3
HFM-183	Koch	PVDF	100 k	493.0
Biomax 100	Millipore	Polyethersulfone	100 k	1377.5
PLHK	Millipore	Regenerated cellulose	100 k	435.1

[a] Referred from internet: http://www.millipore.com/techpublications/tech1/pf1172en00, http://www.sterlitech.com/flat-sheet-membranes-specifications.html#UF.