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

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Nanoporous membranes with superior separation performance have become more crucial with increasing concerns in functional nanomaterials. Here novel ultrahigh permeable nanoporous membranes have been fabricated on macroporous supports by self-assembly of anionic polymer on copper hydroxide nanostrand templates in organic solution. This facile approach has a great potential for the fabrication of ultrathin anionic polymer membranes as a general method. The as-fabricated self-assembled membranes have a mean pore size of 5–12 nm and an adjustable thickness as low as 85 nm. They allow superfast permeation of water, and exhibit excellent size-selective separation properties and good fouling resistance for negatively-charged solutes during filtration. The 85 nm thick membrane has an ultrahigh water flux (3306 l m^{-2} h^{-1} bar^{-1}) that is an order of magnitude larger than commercial membranes, and can highly efficiently separate 5 and 15 nm gold nanoparticles from their mixtures. The newly developed nanoporous membranes have a wide application in separation and purification of biomacromolecules and nanoparticles.

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Introduction

Since the first synthetic ultrafiltration membranes were prepared from nitrocellulose in 1907,[1] nanoporous polymer membranes have been widely used in waste-water treatment, the food industry and life science, and have become more critical with increasing concerns about the living environment and nanomaterials. These processes strongly require membranes with high water flux and good size-selectivity. However, commercial membranes produced mainly by non-solvent-induced phase separation have a thick separation layer with low porosity (general below 10%[2,3]) and broad pore-size distributions, leading to poor cut-off properties, high fouling rates, and low permeation rates.[4–6] The major challenge lies in fabrication of ultrathin high-porous membranes with a uniform pore size distribution, especially with pores of several nanometers.[7,8] For this purpose, researchers focus on how to control precisely the pore size of the membranes, such as block copolymer self-assembly,[9–12] template synthesis,[13,14] supramolecular self-assembly,[15] and the design of coordination polymer networks.[16] Although those approaches have been used to produce nanoporous polymer membranes with good size-selectivity, there is a demand for more permeable membranes in various separation processes.

Very recently, various high-efficiency nanoporous membranes with an ultrathin separation layer on submicron porous supports were reported.[17–25] They have less membrane resistance due to their particular cross-sectional structure and therefore, show ultrahigh water flux. For example, the 60 nm thick crosslinked protein membrane shows a water flux 1000 times higher than commercial ultrafiltration membranes,[17] the 35 nm thick diamond-like carbon nanosheet membrane allows ultrafast organic solvent permeation,[18] and the 22 nm thick graphene nanofiltration membrane has a water flux of 21.21 l m^{-2} h^{-1} bar^{-1}.[19] These works were mainly involved in inorganic membranes.[4,18–21] Although currently most of the commercial membranes are made from polymers, there are rare reports on ultrathin nanoporous polymer membranes.[22–25] Typically, cationic polymer gel membranes were prepared by using a nanofibrous sacrificial layer of cadmium hydroxide nanostrands.[24] Thin film composite membranes were produced by coating a thin polymer film on a nanofibrous scaffold, showing high water flux in ultrafiltration or nanofiltration.[6,22,23] However, till now, there has not been any feasible and versatile approach for the fabrication of highly permeable nanoporous membranes with an ultrathin polymer layer on macroporous supports.

Herein, we designed and fabricated ultrathin self-assembled nanoporous membranes of sulfonated polyetherketone with cardo groups (SPEK-C) using copper hydroxide nanostrand templates. The membranes were applied in separation and purification of biomacromolecules and nanoparticles by

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† Electronic supplementary information (ESI) available: Synthesis and characterization of SPEK-C; effect of the sulfonation degree on membrane formation; structure and properties of the self-assembled membranes; separation of cyt.c by the self-assembled membranes; size-selective separation of gold nanoparticles by the self-assembled membranes; comparison with commercial flat sheet ultrafiltration membranes. See DOI: 10.1039/c3nr03362g

ultrafiltration. Copper hydroxide nanostrands, with a 2.5 nm diameter and several nanometers length, are extremely fine nanofibers that are formed spontaneously in water when the pH of the copper aqueous solution is raised to near neutral.[26] The nanostrands have abundant positive charges on their surface. Negatively charged water soluble solutes, such as dye molecules and proteins, can easily self-assemble on their surface in aqueous solution *via* electrostatic interaction.[17,20] However, it is difficult for water insoluble anonic polymers because the nanostrand dispersion is an aqueous solution. In this work, ultrathin nanoporous SPEK-C membranes were fabricated on a microfiltration filter by self-assembly of SPEK-C chains on the nanostrand templates in organic solution. The resulting membranes show ultrahigh water flux and highly efficient size-selective separation properties in ultrafiltration.

Results and discussion

Polyetherketone with cardo groups (PEK-C) is usually used for preparing separation membranes due to its excellent properties, such as high thermal stability, strong mechanical property, good solvent resistance and film-forming ability.[27] With the introduction of sulfonic groups *via* sulfonation, the resulting SPEK-C has not only the excellent properties of the pristine PEK-C, but also a good hydrophilicity and surface charge effect. Fig. 1a shows the fabrication procedure for making ultrathin self-assembled SPEK-C membranes. Briefly, (i) a copper hydroxide nanostrand solution is filtered to prepare an ultrathin nanostrand layer (Fig. 1b) on a microfiltration filter. (ii) The SPEK-C solution is subsequently filtered through the nanostrand layer to form a SPEK-C coated nanostrand layer (Fig. 1c). (iii) The ultrathin self-assembled nanoporous SPEK-C membranes (Fig. 1d) are finally obtained after removal of the nanostrands. The as-fabricated membranes were applied in the separation and purification of proteins and gold nanoparticles.

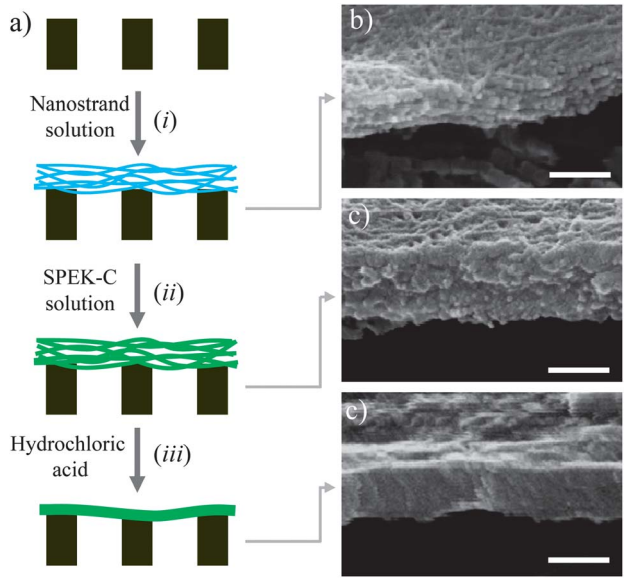

Fig. 1 (a) The procedure for fabrication of self-assembled SPEK-C membranes. (b–d) Cross-sectional SEM images of the nanostrand layer prepared from 3.52 ml cm^{-2} of nanostrand solution, the SPEK-C coated nanostrand layer and the 186 nm thick SPEK-C membrane. The scale bar is 200 nm.

Self-assembly of SPEK-C on the nanostrands

Various SPEK-Cs with different sulfonation degrees (SDs) were synthesized by the procedure described in the previous work (Fig. S1, see ESI†).[28] They are water insoluble and, therefore, the self-assembly process cannot be performed in the nanostrand aqueous solution. SPEK-C chains are supposed to self-assemble on the surface of nanostrands that are embedded in the SPEK-C solution *via* electrostatic interaction. Fig. 2a shows TEM images of the SPEK-C coated nanostrands. The sample was prepared by successively filtering the nanostrand solution and the dilute SPEK-C (0.1 mg ml^{-1}, SD of 0.83) solution across the copper grid. Obviously, the nanostrands are uniform in width, and coated by SPEK-C due to self-assembly of SPEK-C chains on the nanostrand surface. This suggests that anionic SPEK-C would self-assemble on the positively-charged nanostrand surface in the organic solution (Fig. 2b), which is the key to prepare the self-assembled SPEK-C membranes.

The copper hydroxide nanostrands, mono-dispersed in aqueous solution, were filtered on a polytetrafluoroethene membrane (PTFE, 0.2 μm cut-off) to form an ultrathin nanostrand layer. Afterwards, the 0.1 mg ml^{-1} SPEK-C solution with an SD of 0.83 slowly flowed across the nanostrand layer to allow SPEK-C chains to self-assemble on the nanostrand surface (Fig. 3a). The nanostrand layer with a smooth surface is highly porous, and is expected to be dense after self-assembly of SPEK-C chains (Fig. 3b and c). As a result, the pores in the nanostrand layer become narrow and small. The changes in morphology were also observed from the cross-section of the nanostrand layer and its SEPK-C coated counterpart (Fig. 1b and c). That is, voids in the nanostrand layer were filled by the SPEK-C chains that self-assemble on the nanostrands. From these findings, anionic polymers would self-assemble on the surface of the positively-charged templates in organic solution. This suggests that our approach can be a general method to make self-assembled anionic polymer membranes.

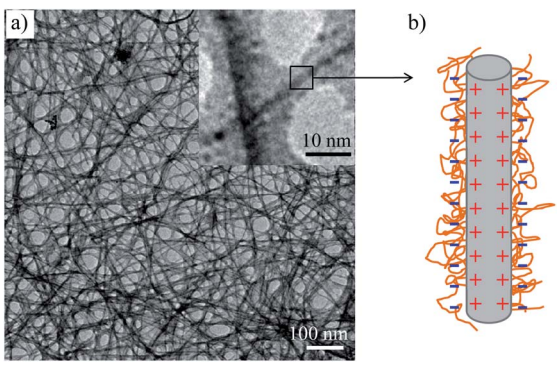

Fig. 2 (a) TEM images of SPEK-C coated nanostrands on a copper mesh. (b) Schematic of self-assembled of SPEK-C chains on the nanostrands.

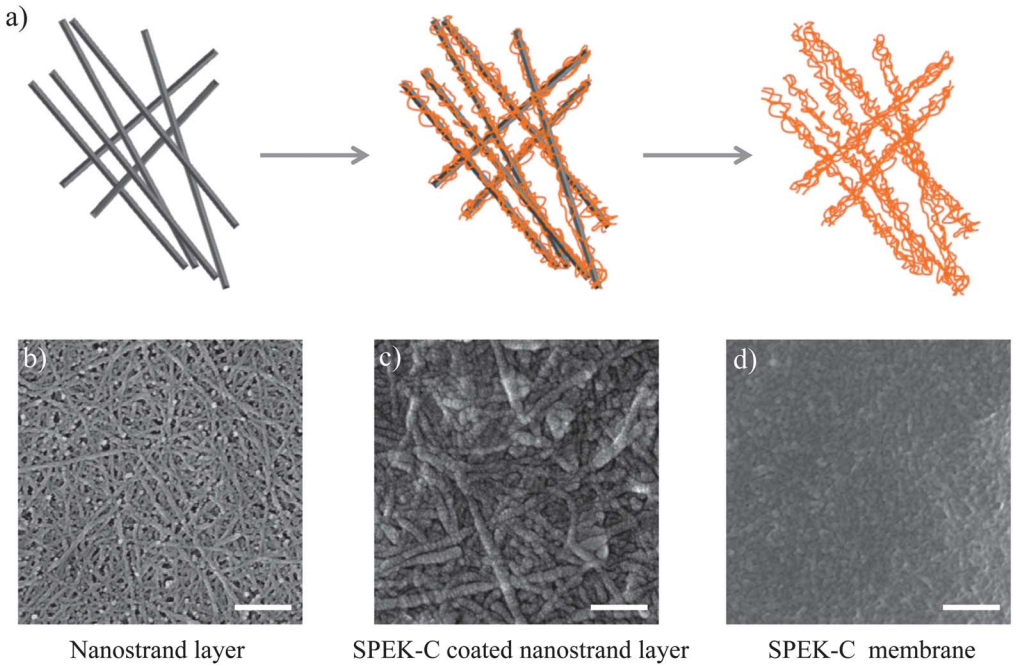

Fig. 3 (a) Schematic of the membrane-formation mechanism. (b–d) Top-view SEM images of the nanostrand layer, the SPEK-C coated nanostrand layer and the SPEK-C membrane. The scale bar is 100 nm.

Formation of self-assembled membranes

As shown in Fig. 1a, the self-assembled SPEK-C membranes were formed after removal of nanostrands. The membrane uniformly covers the PTFE membrane (Fig. 1d). Surprisingly, the membrane with several-nanometer pores is very smooth and highly porous (Fig. 3d). The SD has a significant impact on the formation of self-assembled membranes. Using the template layer prepared from 3.52 ml cm^{-2} of nanostrand solution, the self-assembled membranes cannot be formed on the PTFE membrane below an SD of 0.58, and a self-assembled membrane with few defects can be formed at an SD of 0.71 (Fig. S2, see ESI†). Clearly, the higher the SD, the easier the formation of self-assembled membranes. However, the SPEK-C membrane can be easily swollen in an aqueous solution leading to a weak mechanical strength if the SD is too high. Therefore, we used the SPEK-C with the SD of 0.83 to fabricate self-assembled nanoporous membranes.

With big surface pores of up to 2 μm, the PTFE membrane as a support is uniformly covered by an ultrathin self-assembled membrane (Fig. 4a and b). The membrane thickness can be easily adjusted by varying the filtered volume of the nanostrand solution (*i.e.* the thickness of the nanostrands layer). Five kinds of self-assembled membrane were prepared (Table S1, see ESI†). Ranging from 85 to 414 nm (Fig. S3, see ESI†), the membrane thickness increases almost linearly with the filtered volume of the nanostrand solution (Fig. 4c and d). Of those, the 85 nm thick membrane is the thinnest, and looks dense from the membrane cross-section. From the membrane structure, the ultrathin self-assembled membranes covering a macroporous PTFE support should have ultrahigh water flux in pressure-driven filtration.

Protein separation using self-assembled membranes

To evaluate separation performances of the self-assembled membranes, water flux and protein rejection were measured. Fig. 5a shows water flux, and rejection of bovine serum albumin (BSA) and ferritin by the membranes at neutral conditions. Compared to the commercial membranes (Table S2, see ESI†), the membranes have an ultrahigh water flux that greatly decreases from 3306 to 1417 l m^{-2} h^{-1} bar^{-1} with increasing membrane thickness. With a molecular weight of 66.5 kDa and

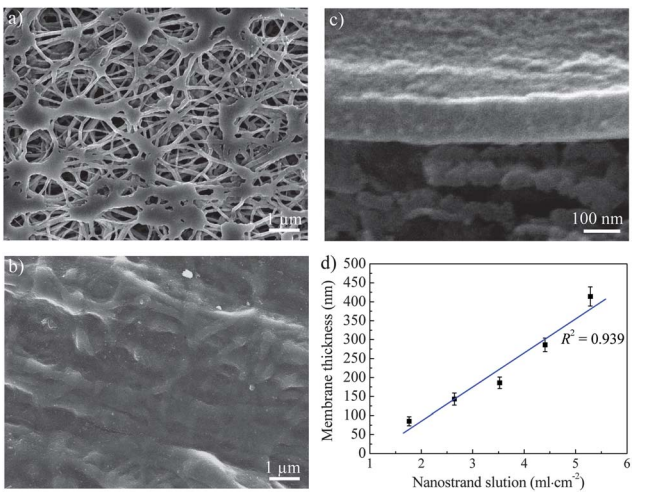

Fig. 4 (a) Top-view SEM images of the PTFE membrane. (b and c) Top-view and cross-sectional SEM images of the 85 nm thick self-assembled membrane respectively. (d) Relationship between the membrane thickness and volume of the nanostrand solution filtered.

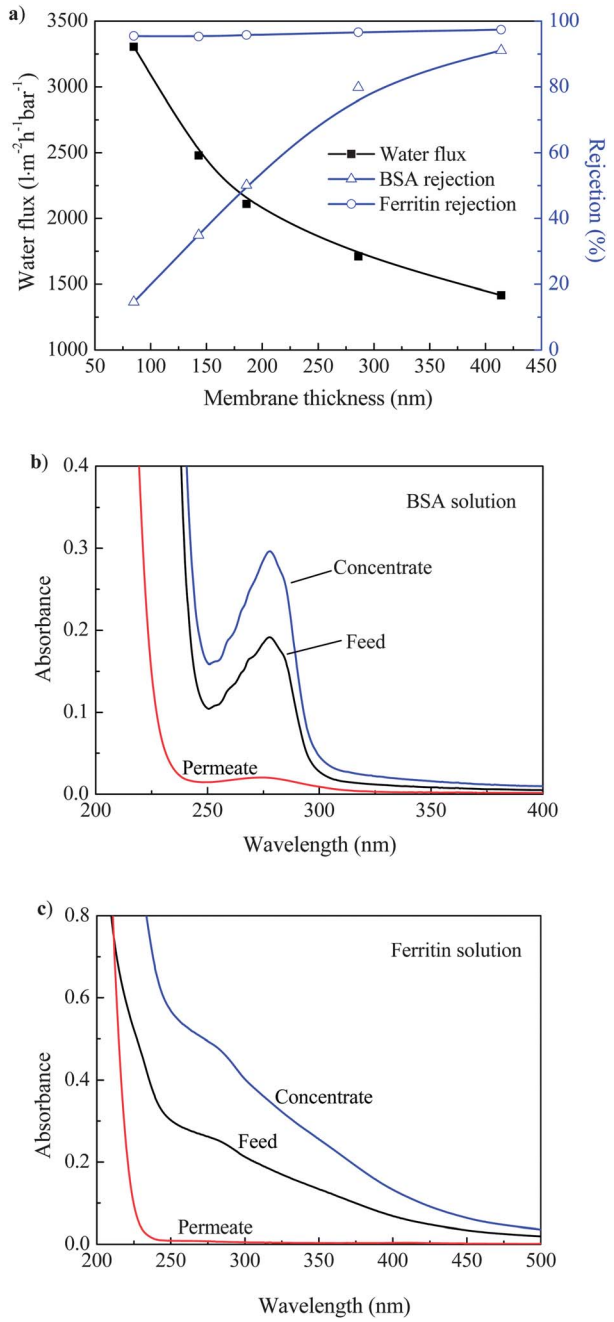

Fig. 5 (a) Water flux, and rejection of BSA and ferritin across the self-assembled membranes. (b and c) UV-vis spectra of the feed, the permeate and the concentrate for separation of BSA solution and ferritin solution by the 414 nm thick self-assembled membrane.

dimensions of $14 \times 4 \times 4$ nm^3, BSA has been widely applied in the biochemical field.[29] Ferritin (450 kDa) with a diameter of 12 nm is a ubiquitous intracellular protein that stores iron and releases it in a controlled manner.[17] It is clear that ferritin rejection is above 95% for all the membranes, and BSA rejection quickly increases with membrane thickness. Of those membranes, the 414 nm thick membrane has the highest BSA and ferritin rejections of 91.1 and 97.4% respectively (Fig. 5b and c), and can separate 5 nm gold nanoparticles with a rejection of 92.5% (Fig. S4, see ESI†).

Generally, protein molecules have a high affinity to the membrane surface and will be adsorbed, leading to membrane fouling and a decrease in water flux.[30] Table 1 lists the properties of the 414 nm thick membrane for separation of protein solution with different pHs. The isoelectric point (pI) of cytochrome c (cyt.c), BSA and ferritin is 10.6, 4.7 and 4.4 respectively. As the feed pH increases, the rejection of BSA and ferritin increases and protein adsorption decreases. This is because the membranes have abundant negative charges, protein molecules are positively-charged when the feed pH is below the pI and negatively-charged when the pH is above the pI. For example, ferritin rejection is 97.4% from the permeate and 97.0% from the concentrate when the feed pH is 6.40, indicating only 0.4% of ferritin molecules being adsorbed on the membrane surface. However, 71.8% of ferritin molecules are adsorbed on the membrane surface at the same filtration condition except that the feed pH is 3.45. On the other hand, the adsorption of proteins on/in the membrane usually results in an increase of rejection. However, the rejection of BSA and ferritin decreases with increasing protein adsorption. This is because SPEK-C chains shrank due to the weak ionization of sulphonic groups at low feed pH, leading to bigger pores of the membranes.[31] This is confirmed by the water flux that greatly enlarges with decreasing feed pH (Fig. S5, see ESI†).

To investigate the effect of protein adsorption in detail, a cyt.c solution (pI of 10.6) was also separated by the 414 nm thick membrane. With a half of the feed (8 ml) being permeated, the rejection is 98.9, 82.0 and 9.5% at the feed pH of 6.30, 10.53 and 11.45, respectively (Table 1). However, the high cyt.c rejection relies on cyt.c adsorption on the membrane. This is observed from the UV-vis spectra of the feed, the permeate and the concentrate of cyt.c solution (Fig. S6, see ESI†). 40 ml of cyt.c solution with pH of 6.30 was filtered across the membrane to study cyt.c adsorption. The cyt.c concentration in the permeate increases with the volume of the permeate, and reaches a constant after 32 ml of the feed being permeated (Fig. S7, see ESI†). That is, the rejection calculated from the permeate first decreases and reaches the constant minimum of ~39%, which is higher than 9.5% (pH of 11.45). Thus, the cyt.c adsorption is completed after 32 ml of the feed being permeated, and it makes the pores smaller.

Size-selective separation using self-assembled membranes

The size, purity and monodispersity of nanoparticles are crucial in determining their optical, electronic and chemical properties.[15] The size-selective separation and purification of metal and semiconductor nanoparticles has thus become increasingly important for fundamental studies and applications. Membrane filtration is a highly efficient and facile alternative, and has drawn increasing attention. As mentioned above, the 85 nm thick membrane with ultrahigh water flux of 3306 l m^{-2} h^{-1} bar^{-1} has a perfect ferritin rejection and low BSA rejection. Thus, this membrane should be able to separate gold nanoparticles of 5 and 15 nm efficiently from their mixtures by filtration.

Table 1 Protein separation properties of the 414 nm thick self-assembled membrane. The pH of the protein solutions was adjusted by 1 mM hydrochloric acid and sodium hydroxide solution

Protein	Cyt.c[b]			BSA			Ferritin		
Size	2.5 × 2.5 × 3.5 nm^3			14 × 4 × 4 nm^3			12 nm diameter		
pI	pH 10.6			pH 4.7			pH 4.4		
pH	6.30	10.53	11.45	3.48	4.68	6.10	3.45	4.36	6.40
Flux (l m^{-2} h^{-1} bar^{-1})	487	534.6	769.6	170.8	193.2	225.1	577.6	643.4	959.4
Rejection (%)	98.9	82.0	9.5	36.6	71.4	91.1	85.1	87.2	97.4
R_{con}[a] (%)	—	—	—	32.7	70.9	81.8	13.3	43.6	97.0

[a] The rejection is calculated from the concentrate. [b] The rejection of cyt.c is resulted from the adsorption of cyt.c on/in the membrane when the feed pH is 6.30 and 10.53.

As shown in Fig. 6a, 5 nm gold nanoparticles will pass across the 85 nm thick membrane whereas 15 nm gold nanoparticles will be rejected. Compared with the feed, the adsorption peak of the concentrate slightly shifts to the right due to the removal of 5 nm gold nanoparticles, and is inverse for the permeate (Fig. 6b). The gold nanoparticle solutions were also characterized using TEM before and after filtration, as shown in Fig. 6c–e. It is clearly visible that the permeate contains only 5 nm gold nanoparticles, however, a few 5 nm gold nanoparticles still remain in the concentrate. The concentration of 5 nm gold nanoparticles in the permeate is 83.0% of that in the feed (Fig. S8, see ESI†). From these findings, the self-assembled SPEK-C membranes have a great potential for highly efficient size-selective separation of nanoparticles.

Conclusions

In summary, we report novel ultrathin self-assembled nanoporous membranes with superior separation performance. They were fabricated on a macroporous support by the self-assembly of anionic polymer on the copper hydroxide nanostrand templates. The facile approach can be a versatile method for preparing ultrathin nanoporous anionic polymer membranes. The results show that the anionic polymer will self-assemble on the positively-charged templates in organic solution. The as-prepared SPEK-C membranes, uniformly covered on PTFE microfiltration membranes, have an adjustable thickness as low as 85 nm. The membranes represent an ultrahigh water flux that is much greater than that of most of commercial

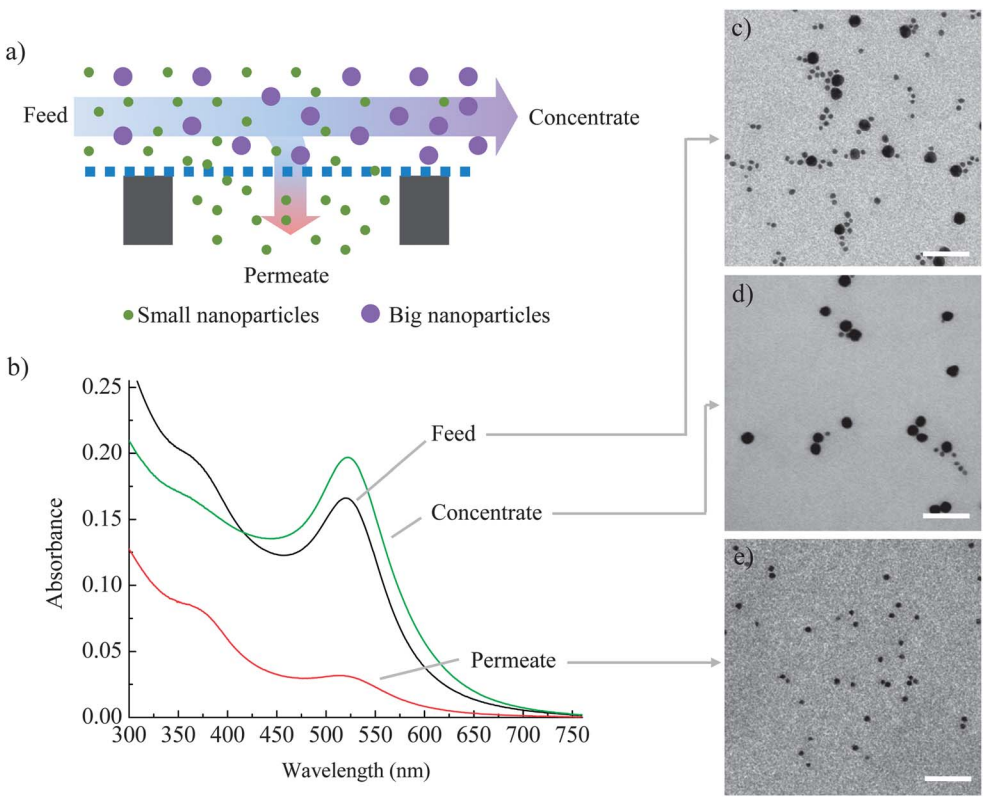

Fig. 6 (a) Schematic of size-selective separation of 5 and 15 nm gold nanoparticles by the 85 nm thick self-assembled membrane. UV-vis spectra (b) and TEM images (c–e) of the feed, the permeate, and the concentrate. The scale bar is 50 nm.

membranes, and have excellent protein rejection. The ferritin rejection is more than 95% for all the membranes. The BSA rejection increases with the membrane thickness, and has the highest value of 91.1%. Meanwhile, the membranes have good fouling resistance for negatively-charged solutes. Further, the membranes have good size-selectivity for separation of nanoparticles. The 85 nm thick membrane shows superfast and high-efficiency separation for 5 and 15 nm gold nanoparticles from their mixture. The newly developed ultrathin nanoporous membranes have a great potential for a wide range of applications in the nanoscience, life science and environmental areas.

Experimental

Membrane fabrication

Five kinds of SPEK-C with various SDs were synthesized by reaction of PEK-C (polymerization degree of 101, Xuzhou Engineering Plastic Factory, China) and sulfuric acid described in the previous work (Fig. S1, see ESI†).[28] The copper hydroxide nanostrand solution was made by mixing an aqueous solution of 1.6 mM aminoethanol and an equivalent volume of 4 mM copper nitrate solution under vigorous stirring and aging for 7 days at 20 °C.[26]

The procedure for membrane fabrication is shown in Fig. 1a. 4–12 ml of nanostrand solution was filtered to form a template layer of nanostrands on a PTFE membrane (0.2 μm cut-off, Millipore) placed on a glass filter holder (Millipore) at a suction vacuum pressure of 80 kPa. The filtration area is 2.27 cm^2. Later on, the 0.1 mg ml^{-1} SPEK-C solution (NMP as a solvent) meandered through the template layer, and then 10 ml of 10 mM hydrochloric acid was filtered to remove the nanostrands of the template layer. The resulting SPEK-C membranes were covered the PTFE membrane uniformly.

Filtration experiments

Filtration experiments were performed using a glass filter holder in dead-end mode. 100 ml of deionized water was filtered across the membrane to measure water flux. Thus, water flux (J, l m^{-2} h^{-1} bar^{-1}) can be calculated by

$$J = V/(Atp) \quad (1)$$

where V is the volume of the water filtered (l), A is the effective membrane filtration area (m^2), t is the filtration time (h), and p is the suction pressure across the membrane (bar).

Proteins (cyt.c, BSA and ferritin, Sigma-Aldrich) were used to evaluate rejection properties of the membranes. 8 ml of protein solution was filtered across the membrane using the glass filter holder. The pH of the protein solutions was adjusted by using 1 M hydrochloric acid or sodium hydroxide solution. The feed, the permeate and the concentrate were characterized using an UV-vis spectrophotometer. The rejection (R, %) is calculated by

$$R = (1 - C_p/C_f) \times 100\% \quad (2)$$

where C_f and C_p are the concentration of proteins in the feed and the permeate, respectively.

The mixture of 5 and 15 nm gold nanoparticles (British Biocell International) was filtered in a similar way to study size-selective separation. This solution was prepared by mixing the diluted 5 nm gold nanoparticle solution and the same volume of 15 nm gold nanoparticle solution. The feed, the permeate and the concentrate were characterized by TEM (JEM 1400).

Characterization

SPEK-C coated nanostrands were characterized by TEM (JEM 1400). The samples for TEM observation were prepared by successively filtering the nanostrand solution and SPEK-C solution across a holey carbon film (Quantifoil® R2/2). The morphology of the membranes was characterized by SEM (Hitachi S-4800). Before observation, a 5 nm thick platinum layer was coated on the sample surface by using a JFC-1600 auto fine coater. UV-vis adsorption spectra were recorded using a Shimazu UV-1800 spectrofluorometer.

Acknowledgements

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