Swelling-induced mesoporous block copolymer membranes with intrinsically active surfaces for size-selective separation†

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Block copolymers (BCPs) are receiving growing interest in the preparation of advanced membranes with regular pores due to their capability to form highly ordered, mesoscopic structures via microphase separation. We report on the fabrication of composite membranes with mesoporous amphiphilic BCPs as the size-selective layer and a macroporous membrane as the supporting layer by coating BCPs onto the supporting membrane. Mesopores were generated in the BCP layer by a selective swelling-induced pore-formation process. The composite membranes showed high pore regularity, strong mechanical robustness, and a separating property that can be tuned simply by changing the swelling time. Furthermore, the polyelectrolyte-natured blocks were exclusively relocated on the pore surface of the BCP layer during the swelling process, rendering an intrinsically active surface on the membrane. As a result, the hydrophilicity and fouling resistance of the membranes were significantly enhanced, and the membranes possessed a reversible pH-sensitive water flux. The membranes were used to separate nanoparticles of similar sizes and it was observed that the membrane subjected to 24 h of swelling was able to discriminate 10 nm gold particles from a mixture containing 2 nm gold particles with 100% yield, demonstrating its superior size selectivity.

1. Introduction

Membrane technology plays an increasingly significant role in producing clean and drinkable water for industry and our daily life by the membrane-based desalination of sea water, purification of contaminated surface and ground water, and treatment and recycling of waste water with high efficiency.1 Improvements in membrane technology could ensure a supply with more affordable clean water for the growing population of megacities through water treatment with enhanced efficiency. For this purpose, advanced membrane systems characterized by mesopores with a narrow pore size distribution and high specific surfaces are particularly attractive. Moreover, mesoporous membranes may have high separation efficiencies related to the possibility of controlling separation processes by interactions with surfaces of mesopore walls.2,3

Commercially available porous membranes are predominantly manufactured by nonsolvent-induced phase separation4 but suffer from wide pore size distributions inherent to the manufacturing process and from the high flow resistance related to high membrane thickness.5 Various techniques have been utilized to fabricate membranes with uniform pore sizes. Track-etched polymer membranes typically suffer from low porosities.6–7 Carbon nanotube membranes8 and silicon nitride membranes9 have only been accessible by tedious and time-consuming preparation processes suffering from low throughput, limitations regarding the membrane area, or difficult device integration. Block copolymers (BCPs) are promising materials for the rational design of thin advanced membranes because they self-assemble into nanoscopic domain structures characterized by well-defined feature sizes.10,11 A number of groups have contributed to BCP-based advanced membranes using BCPs containing degradable blocks, for example, poly(methyl methacrylate) (PMMA),12–14 polylactide (PLA),15,16 and polydimethyldisiloxane (PDMS).17–19 Most synthetic approaches yielding mesoporous BCPs require the chemical degradation of one of the blocks of the BCP,20–22 or the extraction of additives (small molecules or homopolymers) incorporated into the domains of one block.12 As a result, the mechanical stability of the mesoporous BCPs deteriorates, and waste solutions, which are often toxic and/or corrosive, are produced. This degradation/extraction step poses serious problems for the upscaling of the production of BCP-based mesoporous membranes. Moreover, only a limited number of BCPs containing degradable moieties can be employed through this approach and be converted to porous materials via chemical reactions specific to the nature of the BCPs themselves.23–25 Nevertheless, only a few efforts have
been devoted to the development of alternative routes to creating mesoporous BCP membranes. Peinemann, Nunes and coworkers demonstrated an elegant strategy for preparing BCP membranes with highly ordered, monodisperse pores by combining the self-assembly of BCP micelles and the non-solvent-induced phase separation. 26–30 However, the non-solvent-induced phase separation that is involved requires mixing a good solvent for the membrane polymer with a poor solvent. The solvent mixture must be separated again or must be disposed of.

In this work, we report on an environmentally friendly, nondestructive approach to producing mechanically stable BCP-based membranes with sharp size selectivity and active surfaces. In this approach, amphiphilic BCP films were coated on macroporous supporting membranes, and then submerged in a bath of a swelling agent to generate mesopores in the BCP layer via the selective swelling mechanism, resulting in composite membranes with the mesoporous BCP layer as the size-selective layer and the macroporous membrane as the robust supporting layer. After the completion of the selective swelling-induced mesopore generation, the BCP can simply be withdrawn from the swelling agent that can immediately be reused for the next sample. It is even conceivable to design selective swelling-induced mesopore generation as a continuous production process. Moreover, due to the migration of the polyelectrolyte-natured blocks onto the pore wall, the resulting membranes possess an intrinsically active surface with enhanced hydrophilicity, fouling resistance, and even a stimuli–response function.

2. Experimental

Membrane preparation

Polystyrene-block-poly(2-vinyl pyridine) [PS-b-P2VP, Mₙ (PS) = 50 000 g mol⁻¹; Mₙ (P2VP) = 16500 g mol⁻¹; Mₙ/Mₙ (PS-b-P2VP) = 1.09; purchased from Polymer Source Inc., Canada] was dissolved in chloroform at a concentration of 2 wt%. Polyvinylidene fluoride (PVDF) macroporous membrane discs (ϕ = 2.5 cm, Millipore) with a mean pore diameter of 220 nm were used as the supporting membranes. PVDF membranes were soaked in deionized water for several minutes, allowing the water to penetrate into the pores, which prevents the BCP solutions from infiltrating into the pores in the support membrane. The water-filled PVDF membrane was placed on the surface of a clean and dry glass slide. We then dropped one hundred microliters of the BCP solution on the center of the PVDF membrane and carefully forced the solution to spread to the membrane edge using a glass rod to make sure that the entire membrane surface was coated by the solution uniformly. The membrane was quickly transferred to an oven preheated to 130 °C and kept at this temperature for 20 min to evaporate the solvent. The samples were subsequently cooled down to 30 °C and further dried at 30 °C for 2 h. To generate pores in the coated BCP layer, the selective swelling process was applied. 31 Briefly, the BCP-coated PVDF membrane was immersed in ethanol at 60 °C for desired periods of time, followed by air drying in the fume hood at room temperature for at least 2 h after withdrawing the membrane from the ethanol bath.

Characterizations

The surface and cross-sectional morphologies of the samples were examined with a Hitachi S4800 field emission scanning electron microscope operated at 5 kV. In the preparation of the samples for cross-sectional examination, the samples were fractured in liquid nitrogen to obtain fresh cross-sections. Prior to SEM examination, the samples were sputter-coated with a thin layer of gold to enhance their conductivity. XPS measurements were performed on an ESCALAB 250 XPS system (Thermo Scientific) with a monochromatic Al Kα X-ray source and an electron take-off angle of 0°. A survey scan was run in the binding energy range 0–1100 eV, and high-resolution spectra of C 1s, N 1s and O 1s were collected to determine their near-surface contents. A contact angle goniometer (DropMeter A100, Maist) was used to measure the water contact angles of the PS-b-P2VP layer coated on a PVDF membrane before and after ethanol swelling.

Flux, permeation, and adsorption experiments

Permeation experiments were performed at a low stirring speed at room temperature in a stirred cell module (Amicon 8010, Millipore) which featured a 10 mL working volume and an effective membrane area of 4.1 cm². No prewetting of the composite membrane was necessary because the BCP selective layer is adequately hydrophilic to allow for water permeation. However, a 10-minute compaction of the membrane at 0.05 MPa was required to ensure a stable flux. Subsequently, permeation tests were conducted at an operation pressure of 0.02 MPa. Bovine serum albumin, BSA (General Material, with purity >97%), with a molecular weight of 67k and a hydrodynamic diameter of 6.8 nm, dissolved in phosphate buffered solution at a concentration of 0.5 g L⁻¹ was used to characterize the retention properties of the membranes. Concentrations of the feed and filtrate solution were measured via UV absorbance at 280 nm with a UV-vis absorption Spectrometer (NanoDrop 2000c, Thermo). Aqueous solutions of colloidal gold particles with monodisperse particle sizes of 2 nm and 10 nm (BBI international) were mixed and used as the feed solution to test the size-discriminating performance of the membrane subjected to 24 h of swelling. The gold concentrations in the feed, permeate, and retention solutions were determined again using the UV-vis spectrometer. The gold particles in the feed and filtrate were also examined with a JEM-2100 high resolution transmission electron microscope operated at 200 kV. The fouling resistance of the membranes was evaluated by the amount of protein adsorbed onto them. 32 The composite membrane that swelled for 15 h was placed into a weighing bottle filled with 5 mL of 1 g L⁻¹ BSA solution. The weighing bottle was then incubated in a water bath at 25 °C for 12 h to reach equilibrium. The degree of adsorption amount was calculated by comparing the concentrations of the BSA solutions before and after adsorption. The pH-responsive characteristic of the composite membranes was determined for the membrane subjected to 24 h ethanol swelling by monitoring its pH-dependent water flux. Water solutions with different pH values (2–9) adjusted with HCl and NaOH were used. In these tests, the pH of the water medium was gradually increased from 2 to 9 and then reduced from 9 to 2. Before switching to another
water medium, the membrane, as well as the filtration cell, was thoroughly washed with water at the pH to be tested.

3. Results and discussion

Fig. 1 presents the scheme for the fabrication process of the composite membrane with the mesoporous BCP as the selective layer. The PVDF membranes were first submerged in water to fill the pores which was essential to prevent the penetration of the BCP solution into the membrane pores (Fig. 1a). An amphiphilic BCP, polystyrene-block-poly(2-vinyl pyridine) [PS-b-P2VP, $M_n$ (PS) = 50 000 g mol$^{-1}$; $M_n$ (P2VP) = 16 500 g mol$^{-1}$], was dissolved in chloroform at a concentration of 2 wt%. One hundred microliters of the BCP solution was evenly spread on the surface solved in chloroform at a concentration of 2 wt%. One hundred microliters of the BCP solution was evenly spread on the surface. The top layer was a swelling-induced membrane possessed a double-layered composite structure with a entire area of the surface, which corresponded to narrow channels and circular openings, respectively. Although the gaps differed in length they exhibited a similar width of 18 nm. Note that the morphology of the opposite side of the PVDF membrane and its BCP-coated side exhibited a smooth, uniform, and shiny surface, while the opposite side retained its dull appearance as the initially uncoated membrane.

As shown in Fig. 2a and S1 in the ESI†, scanning electron microscopy (SEM) images revealed that the BCP-coated surface subjected to ethanol-swelling for 15 h was composed of twisted and interconnected cylinders. These cylinders were uniform in diameter with an average value of 37 nm and there were gaps with correspondingly twisted morphologies between the cylinders. The gaps were distributed on the surface in mainly two orientations: parallel to the surface and perpendicular to the surface, which corresponded to narrow channels and circular openings, respectively. Although the gaps differed in length they exhibited a similar width of 18 nm. Note that the morphology of the gapped cylinders existed homogeneously throughout the entire area of the surface area. Fig. 2b and c display the cross-section of the membrane at different magnifications. Clearly, the membrane possessed a double-layered composite structure with a thin, mesoporous top layer supported on a thick, macroporous PVDF bottom layer. The top layer was a swelling-induced mesoporous PS-b-P2VP layer with a thickness of ~4 to 7 μm.

Mesopores with a diameter similar to that of the pores on the surface were found to span uniformly throughout the entire thickness of the top BCP layer (Fig. 2c). No interfacial gap along the interface between the BCP layer and the PVDF supporting membrane was observed although the two layers were clearly distinguished from each other, indicating the tight adhesion of the BCP layer to the PVDF membrane. Moreover, some pores on the PVDF membrane immediately below the interface were filled with BCP because of the slight penetration of BCP solution into the water-filled PVDF pores (boxed areas in Fig. 2c and S2 in the ESI†). The filled BCP also showed a featured swelling-induced, interconnected porous morphology. Note that BCP penetration only occurred in the uppermost layers of the PVDF membranes. We believe that this slight penetration of BCP into the PVDF membrane may contribute to further enhancing the adhesion strength between the two layers because of the anchoring effect of the BCP filled in the PVDF pores. We also examined the morphology of the opposite side of the PVDF membrane and found that there were irregular pores with a wide pore size distribution from several tens of nm up to 1 μm, which was the typical pore morphology of the PVDF macroporous membranes (Fig. S3 in the ESI†).

When submerged in hot ethanol, the BCP layer encountered ethanol both from the free top surface and the bottom surface adhering to the macroporous PVDF substrate because ethanol could easily penetrate the PVDF membrane and reach the BCP layer, leading to the selective swelling of the P2VP domains. The swollen P2VP domains expand their size and force the surrounding PS matrix also to have certain plastic deformation, leading to the initially isolated P2VP domains merging to form a

![Fig. 2 SEM images of the a) top view and (b and c) cross-sectional view of the composite membrane at different magnifications, with the PS-b-P2VP layer supported on the macroporous PVDF membrane subjected to ethanol-swelling at 60 °C for 15 h. The boxed areas in c) indicate the penetration of BCP into the PVDF macropores near the PS-b-P2VP–PVDF interface. The scale bars in a) and c) correspond to 1 μm, and the scale bar in b) corresponds to 20 μm.](Image)
increased from (Fig. 1a and 3b–d). For instance, the average pore diameter a greater degree, which led to the formation of larger pores length, they showed nearly identical pore widths of 8 nm. With an increase in the swelling time, the P2VP chains were swollen to a greater degree, which led to the formation of larger pores (Fig. 1a and 3b–d). For instance, the average pore diameter increased from ~15 nm for 4 h of swelling to ~22 nm for 24 h of swelling and reached ~25 nm at a swelling time of 30 h. In addition, the surface of the BCP layer became increasingly coarse at longer swelling times due to a higher degree of swelling, which led to drastic volume expansion and the overflow of the P2VP chains. The continuous tuning of the pore size of the BCP layer is critical because it offers great ease and flexibility in producing membranes with predictably adjustable pore sizes simply by altering the swelling times.

During the swelling process, P2VP chains migrated to the surface and adhered to the pore wall to minimize the surface energy of the system. The presence of the P2VP chains could be demonstrated by water contact angle measurements. The water contact angle of the PS-b-P2VP film before swelling was ~100°, close to that of a PS homopolymer film. In contrast, water droplets on the BCP side of the composite membrane subjected to the swelling-induced mesopore generation process sank into the membrane within several seconds, indicating the strong hydrophilicity as well as the porous nature of the swelling-treated BCP layer. To confirm the migration of P2VP chains onto the surface of the BCP layer after swelling and drying, we used X-ray photoelectron spectroscopy (XPS) to analyze the surface compositions of the BCP layer of the composite membranes before and after swelling. As shown in Fig. 4, three major emission peaks at 284 eV for C 1s, 532 eV for O 1s, and 399 eV for N 1s were observed in the XPS spectra of all the samples. The presence of a small amount of O 1s was due to surface oxygen contamination, which is very common in the XPS analysis. Because nitrogen exists only in the pyridyl groups of the P2VP block, the atomic ratios of nitrogen to carbon (N/C) indicate the contents of P2VP chains on the surface of the membranes. The N/C value of PS-b-P2VP [\(M_n(PS) = 50,000\) g mol\(^{-1}\); \(M_n(P2VP) = 16,500\) g mol\(^{-1}\)] was 3.20%. The surface N/C ratio of the film before swelling was 1.36%, lower than the bulk value of PS-b-P2VP, which implies that PS chains enriched the top surface (air side). The preferential aggregation of PS chains on the air side was because hydrophobic PS had a stronger affinity to air compared to the relatively hydrophilic P2VP. After the film was swollen in ethanol for 1 h, the N/C ratio increased to 4.56%. The increase in the surface N/C ratio confirmed the migration of P2VP chains to the surface of the BCP layer after swelling and drying. Moreover, the N/C ratio increased to 6.25% when the swelling time was extended to 15 h, suggesting that more P2VP chains migrated to the surface with the increase in the swelling degree. The reason for the enrichment of relatively hydrophilic P2VP chains on the surface directly exposed to air is that they are forced to migrate to the surface in the swelling process but lose the mobility to recover back to their initial positions in the drying step in which both the P2VP and PS chains are frozen.

**Fig. 3** SEM images of the surface of PS-b-P2VP membranes subjected to ethanol swelling at 60 °C for different periods of time: a) 1 h, b) 4 h, c) 24 h, and d) 30 h. These images have the same magnification and the scale bar in d) corresponds to 200 nm.

**Fig. 4** XPS wide-scan spectra a) and enlarged spectra b) showing the N 1s peaks of the membranes before swelling and after swelling for 1 h and 15 h.
P2VP chains enriched on the pore surface assume a tunable conformation in aqueous media with different pH levels, leading to a correspondingly tunable effective pore size of the membrane.\textsuperscript{35,36} As a result, the composite membranes were expected to display a pH-dependent water flux. We measured the water flux of the membrane swelling for 24 h as a function of pH (Fig. 5a). There was a significant flux increase when the pH increased from 2 to 9. Interestingly, at pH = 2, no water permeated through the membrane even under an operation pressure of 0.05 MPa, suggesting that the pores in the BCP layer were completely sealed. In stark contrast, the membrane exhibited a water flux as high as ~290 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) at pH = 9 under an operation pressure of 0.02 MPa. As the pH increased, the flux increased smoothly in the range of pH = 2–3. However, there was a drastic increase in the flux of more than 1 order of magnitude when the pH was increased from 3 to 5. Then, the flux increased smoothly again with the increase in pH to 9. Furthermore, the flux decreased to its original value when gradually decreasing the pH from 9 back to 2, indicating that the change in water flux as a function of pH was reversible.

Compared to that of many other pH-sensitive membranes, the sensitivity attained by the change in flux over the given pH ranges of our swelling-induced porous BCP membranes is superior. For example, Zhai \textit{et al.} reported on the preparation of pH-sensitive membranes from P2VP-grafted PVDF by the conventional nonsolvent-induced phase separation technique and observed an approximately twofold increase in flux with the increase in pH from 1 to 6.\textsuperscript{37} Furthermore, the complete closing of pores in the responsive membranes was seldom observed. The superior gating effect of the swelling-induced porous BCP membranes should be attributed to the uniform distribution of the P2VP chains on the membrane pores, almost identical P2VP chain length, as well as the relatively narrow size distribution of the membrane pores.\textsuperscript{28} In conventional approaches to producing pH-sensitive membranes, pH-sensitive polymer chains are localized on the pore surface either by surface segregation during the phase inversion process or by grafting during the surface modification of the preformed membranes.\textsuperscript{38–40} These approaches typically suffer from an inhomogeneous localization of the pH-sensitive polymer chains on the pore surface and also a significant variation in the lengths of the polymer chains dictated by the polymerization mechanism. Consequently, the density, as well as the length of the pH-sensitive chains attached to the membrane pores, varies from pore to pore, a situation that becomes more serious when the pore size exhibits a wide distribution. For instance, for large pores, the attached pH-sensitive chains may not be adequate or long enough to fully cover the entire opening of the pores even in the fully stretched state. This is the reason why the complete closing of pores is hard to observe in these membranes. Additionally, during the selective swelling of block copolymers, P2VP chains segregate to the pore surface during the pore-forming process without the involvement of additional modifiers or any post-modification step. Therefore, the selective swelling approach to the preparation of pH-sensitive membranes is also distinguished from other approaches in terms of simplicity and controllability.

The surface-enriched active P2VP chains provide the membranes with another valuable property: improved antifouling property owing to the relatively high hydrophilicity of P2VP. The protein resistance of membranes is an important property related to their antifouling ability, and lower protein absorption generally indicates better anti-fouling properties. Therefore, we used BSA as a model protein to investigate the antifouling properties of the membranes. The composite membrane swollen for 15 h showed a BSA absorption of ~24 µg cm\(^{-2}\), which was significantly lower than that of a bare PVDF support membrane (54 µg cm\(^{-2}\)) and many other polymeric membranes (typically no less than 30 µg cm\(^{-2}\)).\textsuperscript{41} This was due to the strong hydrophilicity of the BCP layer, which reduced the protein absorption caused by hydrophobic interactions.

We investigated the separation performance of the composite membranes prepared at different swelling times. Fig. 6 shows the pure water flux and retention of BSA for these membranes. Note that no water permeated through the BCP film prior to swelling even when the pressure drop was increased to 0.05 MPa, indicating the nonporous nature of the BCP layer before the swelling process. In contrast, the membrane showed a flux of 100.5 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) after swelling for 1 h, which implied that pores spanning the entire thickness of the BCP layer were obtained after the swelling treatment. After swelling for 4 h, the flux of the
membrane increased to 137.8 L m$^{-2}$ h$^{-1}$ bar$^{-1}$. A further increase in swelling time to 15 h, 24 h, and 30 h led to an increase in flux to 153.7, 238.3, and 312.6 L m$^{-2}$ h$^{-1}$ bar$^{-1}$, respectively. The continuous increase in flux with swelling time was due to the increasing average pore diameter of the BCP layers. However, the increase in flux was not proportional to the swelling time because a prolonged swelling time would also result in an increase in the thickness of the BCP layer, and a thicker BCP selective layer would produce a greater mass-transfer resistance and thus reduced water flux. In contrast, the BSA retention of the composite membranes decreased with the increase in the swelling time. The membrane subjected to 1 h of swelling showed a BSA retention of \( \sim 100\% \), while its water flux remained \( \sim 100.5 \) L m$^{-2}$ h$^{-1}$ bar$^{-1}$, which is typically larger than that of many commercial ultrafiltration membranes with similar retention properties. For the membrane swelling for 4 h, 15 h, 24 h, and 30 h, the BSA retention decreased to 83.4%, 78.6%, 74.6%, and 64.5%, respectively. Similarly, the decrease in the BSA retention with the increase in swelling time was continuous but not proportional because of the competing effect of the increasing pore size and thickness of the BCP layer. As discussed above, both the flux and retention could be tuned over a relatively wide range of values simply by changing the swelling time, implying the high flexibility of the swelling-induced pore generation method in producing membranes with tailor-made separation properties. To investigate the interfacial robustness of the composite membrane, we challenged the membrane subjected to 15 h of swelling with ultrasonication at a frequency of 40 kHz and a power of 100 W for 10 min. The surface morphology of the ultrasonicated membrane showed no observable difference from the membrane prior to ultrasonic treatment under SEM examination. Moreover, the separation properties of the membranes remained unchanged after ultrasonic treatment, thus indicating the strong adhesion between the coated BCP layer and the supporting PVDF membrane.

The composite membranes are promising for use in the separation and fractionation of nanoparticles with similar particle sizes because of their relatively narrow pore size distribution on the BCP selective layer. For example, the membrane subjected to 24 h of swelling retained all of the 10 nm gold particles of a monodisperse colloidal solution also containing 2 nm gold particles, the latter of which permeated the membrane. As shown in Fig. 7a, the feed solution of the mixture of 2 nm and 10 nm gold nanoparticles was red in color, and its UV-vis spectrum displayed a peak centered at approximately 519 nm due to the characteristic plasmonic resonance of the 10 nm gold particles. Meanwhile, the membrane filtrate was colorless and its peak at 519 nm disappeared from the UV-vis spectrum; the retentate showed a red color darker than the feed, and the peak at 519 nm became stronger, indicating that the 10 nm gold nanoparticles were completely blocked by the membrane. However, the colorless filtrate did not necessarily suggest that the filtrate was purely water and free of any gold particles because the 2 nm gold nanoparticles do not have any UV-vis absorption. Therefore, we used transmission electron microscopy (TEM) to examine the size of the gold nanoparticles in the feed and filtrate. Both the 2 nm and 10 nm gold nanoparticles existed in the feed (Fig. 7b), while only the 2 nm particles remained in the filtrate (Fig. 7c), confirming that the 10 nm gold particles were retained and that the 2 nm gold particles permeated through the composite membrane. Considering that commercial membranes typically require a size difference of over 10 times for a species to be effectively separated, the composite membranes with a mesoporous, size-selective BCP layer exhibited a sharp size-discriminating property. One may wonder how the 24 h-ethanol-swollen membrane with a mean pore size of \( \sim 22 \) nm rejects 10 nm sized particles. We have the following explanation to this point. The membrane pore size and gold particle size are measured both in the dried state with electron microscopy techniques. However, they both are in the wet state in the separation operation. P2VP chains are attached on the pore wall and there are also stabilizing organic ligands (e.g. citrate) on the surface of the gold particles. In aqueous environments, both P2VP chains and organic ligands are solvated and partially charged, taking an extending conformation. Therefore, the effective pore size is reduced while the gold particle size is increased. Moreover, interactions between P2VP chains and the surface ligands on gold particles also play a role in determining the separation of gold particles in addition to the size-sieving mechanism. Therefore, it is possible to have a 100% rejection of 10 nm particles using a membrane having a mean pore size of \( \sim 22 \) nm.

4. Conclusions

In conclusion, we have reported on a new strategy for the preparation of composite membranes consisting of a size-selective bicontinuous-mesoporous BCP layer and a macroporous

Fig. 7 a) UV-vis spectra of the feed, filtrate, and retention of the separation of the mixture of 2 nm and 10 nm gold colloidal particles using the membrane subjected to 24 h of swelling, and TEM images of the gold particles existing in the a) feed and c) filtrate of the separation, showing the complete removal of the 10 nm gold particles by the membrane. The insets in a) are the photographs of the feed, retentate, and filtrate solution.
support layer by coating a PS-b-P2VP solution on the surface of a water-filled macroporous support layer, followed by solvent drying and selective swelling in a polar solvent. The BCP layer was ~4 to 7 μm thick and contained mesopores with diameters ranging from a few nm to ~30 nm, tunable by altering the swelling time. Consequently, the flux and retention of the membranes can be tuned over a relatively wide window. The pores on the BCP selective layer were relatively uniform in size, and the membranes were able to completely remove 10 nm gold nanoparticles from a mixture also containing 2 nm gold particles, implying their sharp size-discriminating property. Moreover, P2VP chains relocated to the mesopore walls of the BCP selective layer during the swelling process afforded the composite membranes an intrinsically active surface and consequently enhanced their hydrophilicity and fouling resistance. Additionally, due to the presence of polyelectrolyte-natured P2VP chains on the surface, the membranes possessed a gating effect leading to reversible pH-sensitive water flux.

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