Antifouling ultrafiltration membranes by selective swelling of polystyrene/poly(ethylene oxide) block copolymers

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ABSTRACT

Ultrafiltration (UF) membranes with high permeability and good fouling resistance hold great promise in water treatment and many industry sectors. Herein, antifouling UF composite membranes with mesoporous films of polystyrene (PS)/poly(ethylene oxide) (PEO) block copolymer as the selective layers were produced by the process of selective-swelling-induced pore generation. We spin-coated thin layers of block copolymer onto macroporous supports, and activated the copolymer layers by soaking them in hot ethanol to induce the selective swelling of the PEO microdomains. The porous structures of the block copolymer selective layers can be continuously modulated simply by varying the swelling durations, resulting in UF membranes with water permeabilities adjustable in the range of ~100 to 600 L m⁻² h⁻¹ bar⁻¹. Interestingly, the hydrophilic PEO blocks were enriched on the pore walls after swelling, rendering an inherent fouling resistance to the membranes. Protein fouling tests demonstrated that the membrane exhibited exceptional fouling resistance with a recovery ratio in water flux of nearly 100%. This fouling resistance is expected to be long-standing as the PEO chains are covalently bonded to the membrane matrix.

1. Introduction

As one of the most extensively used membrane technologies, ultrafiltration (UF) is playing an increasingly important role in a wealth of fields such as water treatment, food, biotechnology and molecular sieving [1–3]. Among the various materials to prepare UF membranes, polymers are widely used in virtue of their versatile and tunable properties, excellent process abilities and relatively low costs [4–6]. However, in UF processes, the complicated interactions between the polymeric membranes which are usually hydrophobic in nature and various foulants in the feed solutions frequently result in adsorption and accumulation of foulants on membrane surface as well as in membrane pores. Membrane fouling usually causes sharp decline of fluxes, increase of energy consumption, and reduction of membrane service lifetimes [1,7–9]. Therefore, there is a constant demand in improving the antifouling capabilities of polymeric membranes and developing antifouling UF membranes.

The basic principle of fabricating antifouling membranes is to weaken the interactions between foulants and membranes. According to the entropic effects of dehydration, one of the most efficient methods is to enhance the hydrophilicity of membrane surfaces (including pore walls). The hydrophilic surfaces prevent attaching of foulants to the surface by building a hydration barrier layer with a strong effect of steric repulsion [10,11]. As a water-soluble and electrically neutral polymer, poly(ethylene oxide) (PEO) is well known for its superior resistance to proteins in virtue of its strong water affinity, large excluded volume, and strong coordination capability to water molecules [12,13]. Many studies have demonstrated that PEO chains physically or chemically fixed on the material surface form a surface hydration layer and thus resist the nonspecific adsorption of foreign substances [14,15].

In the past decades, PEO has been extensively employed to enhance the hydrophilicity as well as antifouling properties of membranes targeted to be used in aqueous circumstances [16–20]. A wealth of methods including adsorption, coating, blending, and grafting have been applied to incorporate PEO into membranes. However, the methods of blending and adsorption frequently suffer from the problems of poor adhesion and stability, and inhomogeneous distribution of the PEO in the membrane, which lead to leaching out of the physically trapped PEO chains. In stead, chemical grafting typically requires tedious pretreatments, and/or generates troublesome byproducts and wastes.

PEO-containing block copolymers (BCPs) have recently emerged as a promising precursor to prepare antifouling membranes. BCPs are hybrid polymers consisting of two or more covalently linked homopolymers. They will phase separate in the microscale if the constituent
blocks are thermodynamically incompatible \cite{21,22,23}. Block copolymers of polystyrene (PS) and PEO, that is, PS-b-PEO, have been previously used to prepare membranes through different approaches. Some researchers \cite{24,25} incorporated poly(acrylic acid) (PAA) homopolymers into PS-b-PEO via the hydrogen bonds between PAA and PEO. Pores were formed after the PAA homopolymers were extracted from the assembled PAA/PS-b-PEO membranes. In other cases, PEO moieties in the as-coated PS-b-PEO membranes were etched away by breaking the chemical bonds between the two blocks and porous PS membranes were obtained \cite{26,27}. The extraction/degradation treatment poses significant limits for the upsaling of the membranes. Moreover, after the PEO components are eliminated, the expected antifouling functions will also correspondingly disappear. Another interesting way is to perform self-assembly of block copolymers in the process of nonsolvent-induced phase separation (NIPS) \cite{28,29}. Thus-produced membranes from PEO-containing BCPs may exhibit good fouling resistance because the PEO blocks would segregate on the membrane surfaces during the NIPS process \cite{30}. Unfortunately, antifouling performances of thus-produced membranes have not yet been reported.

Recently, we discovered that nanoporous membranes can be facilely prepared by swelling BCPs in selective solvents to the minority blocks, which is known as the selective-swelling-induced pore generation \cite{31,32}. Interestingly, simultaneously to the pore formation, the minority polar blocks are enriched on the pore walls, producing membranes with outer surfaces and pore walls homogenously covered by the minority blocks. We clearly demonstrated the presence of polar blocks, mainly polyvinylpyridine (PVP), on the membrane surfaces by a number of surface analyses \cite{33,34,35}. Specifically, we prepared thin PS-b-PEO nanoporous films supported on silicon substrates by selective swelling. Adsorption tests showed thus-produced nanoporous films exhibited nearly zero adsorption to proteins because of the surface enrichment of PEO chains \cite{36}. We note that selective swelling has been explored to produce UF membranes predominantly from PS/PVP block copolymers in our previous works \cite{33,34,35}; however, selective swelling of PEO-containing BCPs has not yet been explored to prepare separation membranes. More importantly, the antifouling properties of thus-produced membranes of PEO-containing BCPs have never been touched before although excellent fouling resistance can be expected. Selective swelling of PEO-containing BCPs may open a new and easily accessible avenue to produce antifouling UF membranes.

In this work, we prepared antifouling UF composite membranes by selective swelling of PS-b-PEO block copolymers deposited on macro-porous supports. PS-b-PEO films were firstly spin-coated on macro-porous PVDF substrates, and then soaked in hot ethanol to create mesopores in the block copolymer layers, producing composite membranes with mesoporous block copolymer as the selective layer supported on the macro-porous substrate. The mesoporous PS-b-PEO separation layer is typically around one micrometer in thickness, providing a high permeability to the composite membrane. Protein fouling tests demonstrated the exceptional fouling resistance of the membranes as a result of uniform, dense lining layers of PEO chains along the pore walls. Selective swelling of PEO-containing BCPs to prepare antifouling membranes is extremely simple and highly controllable as no chemical reactions are involved. Moreover, as the PEO chains are covalently bonded to the membrane matrix, the fouling resistance is expected to be long-standing, and will not diminish during applications which is a frequent problem for antifouling membranes prepared by the blending or adsorption methods.

2. Experimental

2.1. Materials

Polystyrene-block-poly(ethylene oxide) (PS-b-PEO, abbreviated as SEO) below, \(M_n(PS) = 42,000\) g mol\(^{-1}\), \(M_n(PEO) = 11,500\) g mol\(^{-1}\), PDI \(= 1.07\) was purchased from Polymer Source Inc., Canada, and was used as received. Discs of macroporous polyvinylidene fluoride (PVDF) membranes (\(d = 2.5\) cm, mean pore diameter \(= \sim 220\) nm) were ordered from Millipore and served as the supporting substrates. Chloroform and ethanol in the analytical grade were supplied by local suppliers. Bovine serum albumin (BSA, Aladdin, Fraction V), with a molecular weight of 67 kDa was dissolved in phosphate buffered salines (PBS, at the physiological pH of 7.4) to prepare protein solution with the concentration of 1 g/L.

2.2. Characterizations

The surface and cross-sectional morphologies of SEO composite membranes were examined with a field emission scanning electron microscope (S-4800, Hitachi) operated at an accelerating voltage of 5 kV. Before SEM examination, the specimens were sputter-coated with an ultrathin layer of platinum to enhance the conductivity of samples by high vacuum evaporation.

2.3. Preparation of composite membranes

The SEO solution with a concentration of 2 wt% was prepared by dissolving a desired amount of SEO in chloroform. We used 0.22-µm PTFE filters to filter SEO solutions three times to remove any big aggregates. Composite membranes were produced by spin-coating the SEO solutions on PVDF substrates. Before spin-coating, PVDF substrates were immersed in deionized water for a few minutes, permitting water to fill into the pores of the PVDF supporting membranes. There was water remaining on the surface of the PVDF substrate when it was removed from water. We gently placed the water-filled PVDF substrate on the surface of the glass slide, and water remaining on the PVDF surface helped to attach PVDF on the surface of the glass slide. 30 µL of the SEO solution was dropped on the PVDF substrate, followed by spincoating at 5000 rpm for 20 s with a speed of 5000 rpm. After spincoating, the sample was heated at 80 °C for 20 min to evaporate the solvent and water in vacuum. To create mesopores in the coated SEO layer, the sample was subsequently soaked in ethanol at 65 °C to perform the selective-swelling-induced pore-making process for desired durations, followed by air drying at room temperature. Fig. 1 gives the scheme for the preparation of the composite membranes.

2.4. Filtration tests

The water permeability and BSA rejection of the SEO composite membranes were measured in a filtration cell (Amicon 8010, Millipore) with a 600 rpm stirring speed. Before testing, a 20-min compaction to the membrane at 1 bar was used to stabilize the permeability. BSA was used to probe the rejections of the membranes. The permeability \(J_w\) and BSA rejection \(R\) were calculated by following Eqs. (1) and (2), respectively.

\[
J_w = \frac{V}{A \Delta t \rho} \tag{1}
\]

where \(V\) (L) is the volume of permeated water, \(A\) (m\(^2\)) is the effective area of the membrane, \(\Delta t\) (h) is the permeation time, and \(p\) (bar) is the operation pressure.

\[
R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}
\]

where \(C_p\) and \(C_f\) are BSA concentration of permeation and feed solution, respectively. \(C_p\) was maintained at 1 g/L, while \(C_f\) was sampled in permeation solution after BSA ultrafiltration. To test the membrane pressure-resistant property in water, the water fluxes were tested at 0.2, 0.5, 0.8, 1.0, 1.5, 2.0 and 2.5 bar, respectively. The BSA concentrations in permeate and feed were measured by a UV–vis spectrophotometer (NanoDrop 2000c, Thermo) at the wavelength of 280 nm.
2.5. Evaluation of fouling resistance

To investigate the antifouling properties of composite membranes, the membrane was challenged with BSA aqueous solutions. The fouling tests were performed by alternately feeding pure water and the simulated pollutant solution, BSA (1 g/L, pH 7.4), in the filtration cell with stirring at 600 rpm to minimize concentration polarization. Firstly, original water permeability was recorded as $J_1$, then the feed was changed to the BSA solution and stable flux was recorded as $J_p$. The membrane was then washed with water for 10 min and secondary pure water flux was recorded as $J_2$. The water flux recovery ratio (FRR) and the corresponding irreversible fouling ratio (IFR) were estimated using Eqs. (3) and (4), respectively:

$$\text{FRR} = \frac{J_2}{J_1} \times 100\% \quad (3)$$

$$\text{IFR} = 1 - \text{FRR} \quad (4)$$

The alternative filtrations of water and BSA solutions were cycled for three times to test the antifouling durability of the composite membranes. Each filtration cycle was divided into alternative filtrations to pure water, the BSA solution and the pure water again, which were identical to the process described above.

3. Results and discussion

3.1. Morphology of the SEO composite membranes

In the preparation of composite membranes, heating at 80 °C in vacuum was used to evaporate the solvent and water and also to improve the adhesion between the SEO layer and the PVDF substrate. The enhanced adhesion ensures the structural integrity of the SEO/PVDF composite structures during the following ethanol swelling, and no detachment or cracking could be observed after swelling. The SEO-coated side of the composite membranes displayed a homogeneous and shiny appearance whereas the other side maintained the original dull appearance (Fig S1). SEM examinations reveal that the as-coated SEO film exhibited a nonporous morphology with a dense surface and the thickness of the SEO layer was ~ 500 nm (Fig S2). After immersing the composite membrane in ethanol at 65 °C for 8 h and subsequent air drying at room temperature, pores appeared in the membrane surface (Fig. 2b). These pores are mainly in the circular or elongated shapes, and their pore sizes can be roughly estimated to be ~ 34 nm by considering the pore widths of elongated pores as their pore diameters. The large-field SEM image shown in Fig. 2a reveals that these pores are uniformly distributed throughout the surface of SEO layer. As shown in the cross-sectional SEM image (Fig. 2c), the membrane exhibited a bilayered morphology consisting of a thin mesoporous layer on top of a thick macroporous bottom layer. The top layer was the mesoporous SEO with a thickness of ~ 1 μm (Fig. 2c and S3). There is an increase in the thickness of the SEO layer after swelling. This is due to the non-destructive formation of pores in the SEO layer by selective swelling as we also observed in the selective swelling of other BCP films [31–33]. The formation of pores will increase the volume of the SEO layer. Because the SEO layer is tightly confined to the PVDF substrate the volume expansion can only take place in the $z$ direction, resulting in the increase in the thickness. As shown in the cross-sectional SEM image in Fig. 2c, there were also mesopores homogeneously distributed throughout the entire SEO top layer. Moreover, it should be noted that, we could not observe any interfacial gap along the interface between the two layers although the two layers were clearly distinguished from themselves, indicating a strong adhesion between them. Besides, as highlighted in the boxed area in Fig. 2c, penetration of the SEO solution into the substrate pores also slightly happened, leading to partial filling of the copolymer into the pores of the PVDF substrate near the interface. This slight penetration of SEO into PVDF substrate is desirable as it further improves the adhesion between the SEO layer and PVDF substrate. In addition, we examined the uncoated side of the composite membrane and found that it remained a typical morphology of the macroporous PVDF substrate (Fig S4). No filling of materials could be found on this side, confirming that the SEO coating solution did not leak to the bottom side of the substrate.

The pores in the SEO layer are formed through the mechanism of selective-swelling-induced pore generation [31,32]. The volume fraction of PEO in SEO used in this work is approximately 21.5%. According to the phase diagram of block copolymers [23], the PEO blocks form cylinders randomly scattered in the matrix phase of PS in the as-coated SEO layer. In the swelling process, ethanol diffuses into and selectively enriches in PEO cylinders as ethanol is a good solvent to PEO but a nonsolvent to PS. With the uptake of ethanol in PEO cylinders, osmotic pressure is accumulated and PEO cylinders are expanded in size, leading to the plastic deformation of the glassy PS matrix. The expanding PEO cylinders contact and are merged with their neighbors, resulting in a continuous phase of swelling PEO domains distributed in the PS matrix. When the SEO composite membranes are removed from the swelling bath, with the evaporation of ethanol the deformed PS chains are frozen as they are in the glassy state. Meanwhile, the swollen PEO chains collapse, producing pores along the positions where the expanding PEO domains are initially occupied. The collapsed PEO chains are covered along the pore walls as they are covalently linked to the PS chains which constitute the matrix of the SEO layer.

The pore sizes of the SEO layer can be tuned by a number of parameters such as compositions (molecular weights, block ratios, etc) of the block copolymer and the swelling conditions (solvents, temperatures, durations, etc), and the swelling duration is an easy measure can be conveniently changed [33]. We investigated the morphology of the SEO composite membranes prepared with different swelling durations. As we mentioned earlier, before swelling the as-coated SEO layer was nonporous. With a swelling duration of 1 h, narrow channels or
A circular opening appeared in the surface of the SEO layer (Fig. 3a). The channel-like pores exhibited nearly identical pore widths of \( \sim 17 \) nm although they differed in length. With increased swelling durations, PEO microdomains were swollen to larger degrees, leading to bigger pores (Fig. 3b–d). The average pore size was enlarged from \( \sim 24 \) nm for 2 h of swelling to \( \sim 28 \) nm for 4 h’s swelling, and reached \( \sim 30 \) nm after swelling for 6 h. The continuous tuning in pore size is very much desired as it provides high flexibility and ease in preparing membranes with predictable pore sizes and separation properties conveniently by adjusting the swelling durations. Additionally, the pore sizes can also be tuned by altering the swelling temperatures. In general, lower swelling temperatures produce smaller pores. As shown in Fig. S5, swelling at 50 °C for 12 h results in a porous morphology similar to swelling at 65 °C for 8 h. It should be noted that the pore sizes discussed here are determined by SEM imaging on dried samples, which will become smaller when the nanoporous SEO layers are used in aqueous environments for membrane separations because of the swelling effect of the PEO chains attached to the pore walls. This change in pore sizes has been discussed in our previous study [36].

3.2. Separation performances

We then explored the separation performances of the SEO composite membranes prepared by swelling with different durations. The permeability of the bare, uncoated PVDF substrate is \( \sim 6000 \) L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). After spincoating with SEO, it exhibited no water permeability under a pressure of 0.5 bar for at least 10 min, implying the defect-free nature of the coating SEO layer. In contrast, after swelling in ethanol, water permeability was generated. Fig. 4 presents the pure water permeability and rejection of BSA of the membranes. After swelling for 30 min, the SEO composite membrane showed a permeability of 97 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), confirming that the pores generated in the SEO layer are interconnected and water-permeable. After swelling for 1 h, the permeability was increased to 136 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). The swelling duration of 2 h, 4 h, 6 h, 8 h and 12 h led to continuously increased permeability of 287, 368, 395, 474 and 600 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), respectively. The progressive increase in water permeability was due to the ever-enlarged pores in the SEO layer with the swelling duration. However, we note that there was no a linear relationship between water permeabilities and swelling durations.

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Fig. 2. SEM images of an SEO composite membrane with the SEO layer on top of the macroporous PVDF substrate prepared by ethanol swelling at 65 °C for 6 h: (a, b) top view at different magnifications, (c) cross-sectional view. The boxed area in (c) indicates the filling of SEO into the PVDF macropores near the bi-layered interface.

Fig. 3. SEM images of the surface of SEO composite membranes prepared by ethanol swelling at 65 °C for different durations: (a) 1 h, (b) 2 h, (c) 4 h, and (d) 6 h, respectively. These images have the same magnification and the scale bar corresponding to 300 nm is given in (a).
because an extended swelling duration would also increase the thickness of the SEO layer (Fig S6) that would result in larger resistance in mass transfer. Oppositely, the BSA rejections of the SEO composite membranes exhibited a decreasing tendency with prolonged swelling duration. The membrane subjected to 30 min of swelling exhibited a 94.4% rejection to BSA which has the size of ~ 14 nm × 3.8 nm × 3.8 nm [37]. For the membrane prepared with a swelling duration of 2 h, 4 h, 6 h, 8 h and 12 h, the BSA rejections was decreased to 94.2%, 77.2%, 58.5%, 56.1%, 31.1%, and 19.4%, respectively. Similarly, the reduction of the BSA rejection with increasing swelling duration was also continuous but not linear as a result of the competing effect between the enlarged pores and thickened SEO layer. As we mentioned previously, both permeability and rejection could be adjusted within a quite wide range simply by altering the swelling duration, suggesting the great convenience of the process of selective-swelling-induced pore generation in making tailor-made UF membranes. Moreover, considering that the nanoporous SEO layer is currently ~ 1 µm in thickness which can be further reduced by using SEO solutions with lower concentrations, we expect that the permeability of the composite membranes can thus be improved at low or no cost of rejection as rejection is mainly determined by the pore sizes of the selective layers.

3.3. Mechanical stability

The mechanical strength of the SEO composite membrane was investigated by measuring the pure water fluxes at various transmembrane pressures (TMPs) from 0.2 to 2.5 bar. Fig. 5 reveals that there is a linear relationship between pure water fluxes and TMPs in this range. The composite membrane can tolerate a pressure as high as at least 2.5 bar and does not break as there is no sudden increase in water flux under the pressure up to 2.5 bar. Moreover, the SEO layer would not fall off or fracture, even if we curved the SEO composite membrane (Fig S7). Therefore, we conclude that the SEO composite membranes possess an excellent mechanical strength upon compositing with the PVDF substrates.

3.4. Antifouling properties

We carried out dynamic permeation tests of BSA protein to evaluate the fouling resistance of the produced composite membranes. In the dynamic filtration tests, pure water, the BSA solution, and pure water were successively fed into the SEO composite membrane, and the corresponding permeabilities were recorded. As can be seen in Fig. 6, the SEO composite membrane prepared by swelling at 65 °C for 8 h showed an initial water permeability of ~ 384 L m⁻² h⁻¹ bar⁻¹. When the BSA solution was fed, the membrane exhibited a reduced permeability of ~ 322 L m⁻² h⁻¹ bar⁻¹. However, it is apparent that the time-dependent BSA permeability profiles exhibited a stable tendency and did not show a rapid decline within 100 min. The membrane was then washed with deionized water to clean the foulants for 10 min and its permeability to pure water was tested again. Clearly, the water permeability was fully recovered to the initial value, implying an exceptional fouling resistance with an FRR of ~ 100% and correspondingly an IFR of ~ 0%. The superior antifouling property of the SEO composite membrane should be ascribed to the enrichment of the hydrophilic PEO chains on the membrane surfaces including pore walls [38]. That is to say, the surface-enriched PEO chains prevent the foulant accumulation on the surface of the SEO composite membrane which leads to significant severe concentration polarization as well as membrane fouling [39].

The long-term fouling resistance of the prepared membrane was also investigated. As shown in Fig. 6, three cycles of filtration tests were employed to evaluate the durability of antifouling properties. It is observed that the IFR of the SEO composite membrane prepared by swelling at 65 °C for 8 h was ~ 0%, and the FRR after simply pure water washing was ~ 100% throughout the three cycles of tests. It implies that the fouling resistance of the SEO composite membrane remained stable after three cycles of filtration and had durability in long-time operations.

Typically, UF membranes prepared by using PEO-containing polymers as the hydrophilic modifiers [40–42] or by grafting with PEO derivatives [43] exhibit FRRs varied in the range from 60% to 90%, and a FRR of 100% has seldom been reported. Moreover, the fouling
resistance of our membranes is expected to be long-standing because the PEO blocks would not leach out as they are covalently bonded to the PS blocks consisting of the membrane matrix. This long-standing hydrophilicity and fouling resistance are a special advantage of the PS-b-PEO membranes prepared by the selective swelling strategy and very much desired because foreign additives physically incorporated into the membranes frequently suffer from leaching out during operations, leading to decay and loss of fouling resistance with time [44].

Such an exceptional fouling resistance should be ascribed to the synergetic effects of the following reasons. Firstly, the PEO chains are homogeneously tethered throughout the outer and inner surfaces of the membranes. Secondly, the PEO chains have a molecular weight of 11,500 g mol−1, leading to a dense PEO hydration layer along the pore wall. Thirdly, the PEO chains are covalently bonded to the PS blocks consisting of the membrane matrix, which would not leach out during applications and promising long-standing fouling resistance. In contrast, for the membranes prepared by incorporating PEO homopolymers as hydrophilic modifiers, the PEO chains cannot fully segregate to the pore wall to form a uniform layer because of the kinetic limitation in the fast phase inversion process. Moreover, the used PEO homopolymers usually have a low molecular weight, typically smaller than 5000 mol−1, and it may be difficult for them to form a dense, defect-free hydration layer. In addition, the low-molecular-weight PEO homopolymers are prone to be released from the membrane matrix as they are weakly anchored to the membrane matrix via physical chain entanglement. It is known that PEO is prone to oxidative degradation [45], which may lead to the eventual loss of the covalently linked PEO chains and correspondingly the deterioration of the fouling resistance. However, it is expected that the complete degradation of such long PEO chains used in our study takes longer time than PEO chains with relatively low molecular weights. Therefore, the fouling resistance of the membranes prepared in the present study is expected to maintain for longer durations.

4. Conclusions

SEO block copolymer composite membranes consisting of size-tunable 3D interconnected mesoporous SEO selective layers and macroporous supporting layers were produced by the process of selective swelling-induced pore generation. The SEO layer was typically less than 1 µm in thickness and hosted interconnected mesopores with diameters tunable by altering the swelling duration. The water permeabilities and BSA rejection of the composite membranes can be adjusted within a relatively wide range. Meantime, the SEO composite membranes showed a good mechanical strength. Moreover, the hydrophilic PEO blocks were selectively enriched onto the pore walls of the SEO selective layer, affording the membranes superior fouling resistance. For the SEO composite membrane prepared at 65 °C for 8 h, the flux decline rate was extremely low and the flux recovery ratio was up to ~ 100% in the antifouling test. A stable and durable antifouling property after three cycles of BSA filtration was also confirmed in our work. This study contributes a facile strategy to producing highly permeable UF membranes with excellent fouling resistance which are strongly desired in water treatments.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2017.08.015.

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