

Zwitterions coated hollow fiber membranes with enhanced antifouling properties for osmotic power generation from municipal wastewater



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ABSTRACT

Fouling on pressure-retarded osmosis (PRO) membranes leads to severe declines in water flux and power density because their porous substrates are facing the wastewater feed. Thus, inorganics, organics and microorganisms in the wastewater are prone to depositing on the substrate surface and even in its pores. In order to reduce the fouling propensity, coating the substrate surface of PRO membranes with zwitterionic materials proves to be an effective way. In this work, 2-methacryloyloxyethylphosphorylcholine (MPC), is modified and grafted onto the polydopamine (PDA) coated poly (ether sulfone) (PES) hollow fiber substrate. Both the synthesis and surface coating of MPC are easy and facile to be scaled up. Compared with the pristine PES and PES-PDA substrates, the MPC modified substrate (PES-PDA-MPC) exhibits high resistance to protein adsorption as well as bacteria adhesion. By using a state-of-the-art thin-film composite poly (ether sulfone) (TFC-PES) hollow fiber membrane as the control for power generation, the power density of the TFC-PES-PDA-MPC membrane can achieve as high as 7.7 W/m² while the unmodified one has only 6.0 W/m² after 3 h's PRO tests. In conclusion, the osmotic power generation of PRO membranes can be significantly sustained by modifying the membrane surface with zwitterions.

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1. Introduction

The rapid increases in energy consumption and CO₂ emissions have accelerated the exploration of renewable and green energy (Evans et al., 2009). Among them, osmotic energy released from the mixing of water streams with different salinities via pressure retarded osmosis (PRO) has attracted global attention owing to its abundance and renewability (Achilli et al., 2009; Alsvik and Hägg, 2013; Gerstandt et al., 2008; Han et al., 2015; Kim et al., 2015; Ramon et al., 2011). In a typical PRO process, water from the low salinity solution (i.e., feed solution) can spontaneously pass through a semi-permeable membrane to the high salinity solution (i.e., draw solution) due to their chemical potential difference. Consequently, the salty water compartment has an expanded volume with a higher pressure. By releasing the pressurized draw solution through a hydro-turbine, one can harvest electricity as the osmotic energy.

Two factors primarily affect the productivity of a PRO process; namely, the PRO membrane and the feed pair. An ideal PRO membrane requires a high water permeability, high salt rejection, low concentration polarization, high mechanical strength, and minimal fouling tendency. During the last decade, a significant progress has been made on PRO membranes in the configurations of flat-sheet (Bui and McCutcheon, 2014; Cui et al., 2014; Li et al., 2012, 2013; Song et al., 2013; Yip et al., 2011) and hollow fiber (Chou et al., 2013; Han et al., 2013, 2015; Li and Chung, 2014; Sun and Chung, 2013; Zhang and Chung, 2013). In case of feed pairs, in addition to the conventional pair of river water and seawater, the feed pair of concentrated reverse osmosis (RO) brine and wastewater from municipal recycle plants has received great attention because it has a higher salinity gradient and can potentially produce a higher power density (Achilli and Childress, 2010; Altaee and Sharif, 2015; Chung et al., 2015; Han et al., 2015; Kim et al., 2015; Li and Chung, 2014; Sun and Chung, 2013; Thorsen and Holt, 2009; Wan and Chung, 2015, 2016; Zhang and Chung, 2013). In addition, this new feed pair may add extra values such as lowering the overall energy consumption for RO (Chung et al., 2015; Wan and Chung, 2016), diluting the seawater RO brine for

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ecologically-friendly disposal (Chung et al., 2015; Han et al., 2015) and saving some seawater pretreatment costs (Achilli et al., 2009). However, the new feed pair also creates challenges.

It is known that membrane fouling due to the deposition of inorganic and organic materials and microorganisms onto its surface and pores leads to a rapid decline of power density (Mi and Elimelech, 2010; Xie et al., 2013), but the situation becomes more severe if the wastewater from municipal recycle plants is used as the feed (Chen et al., 2016, 2014, 2015; Gu et al., 2013; She et al., 2013; Wan and Chung, 2015; Zhang et al., 2014). Wan et al. managed to obtain a maximum power density as high as 27 W/m² using 1 M NaCl solution and de-ionized water as the feed pair (Wan and Chung, 2015). However, the power density declines fast if de-ionized water was replaced by the municipal wastewater. The fouling not only affects the membrane performance adversely, but also increases the operation cost because of the need for frequent cleaning and maintenance (Chen et al., 2015; She et al., 2013). This necessitates the development of PRO membranes with superior antifouling properties.

Many antifouling methods have been developed for conventional microfiltration, ultrafiltration and RO membranes (Kang and Cao, 2012; Lei and Ulbricht, 2014; Rana and Matsuura, 2010; Escobar and Van der Bruggen, 2011). However, only limited antifouling strategies have been proposed to enhance the anti-fouling properties of PRO membranes. This is due to the fact that fouling occurs differently between PRO and conventional membranes. In RO membranes, fouling mainly takes place on the outer surface of the selective layer, while fouling may occur severely on and in the porous substrate as well as just beneath the selective layer of PRO membranes (Xiong et al., 2016). In addition, challenges may arise from (1) the complexities of internal concentration polarization and reverse salt flux in PRO and (2) the balance among hydrophilicity, mechanical strength, and power density during membrane modifications. One must only modify the porous substrate without sacrificing the mechanical strength and power density. Li et al. developed a dendritic hyperbranched polyglycerol anchored PRO membrane, which is able to reject proteins and bacteria, but not inorganic scaling (Li et al., 2014). Therefore, in the later study, they functionalized the hyperbranched polyglycerol polymer with negatively charged functional groups (Li et al., 2016). Recently, Cai et al. designed a zwitterionic copolymer modified PRO membrane with superior fouling resistance to nonspecific foulants (Cai et al., 2016). Zwitterion is a molecule which contains both positive and negative functional groups while the overall charge neutrality is maintained. It has received increasing attention recently due to its excellent anti-adhesive properties against protein and bacteria (Yu et al., 2014; Zheng et al., 2016). However, the procedures for the synthesis of the zwitterionic copolymers are complicated that may hinder the module scale-up.

Therefore, it is imperative to find simple and effective zwitterions for the surface modification of PRO membranes in order to accelerate the commercialization of PRO for osmotic pressure generation. To meet this objective, this work aims (1) to design and fabricate zwitterionic material coated PES hollow fiber membranes by both simple synthesis and coating approaches, and (2) to investigate their anti-fouling properties for osmotic power generation using wastewater from municipal recycle plants. A state-of-the-art thin-film composite poly (ether sulfone) (TFC-PES) hollow fiber membrane was employed in this study for various surface modifications. As shown in Fig. 1, we incorporated 2-methacryloyloxyethylphosphorylcholine (MPC) on the outer surface (i.e., the substrate surface) of TFC-PES membranes via three steps: (1) The outer surface of TFC-PES membranes was treated by polydopamine (PDA) to obtain PES-PDA; (2) MPC was first converted to thiolated-2-methacryloyloxyethyl phosphorylcholine (MPC-SH) in

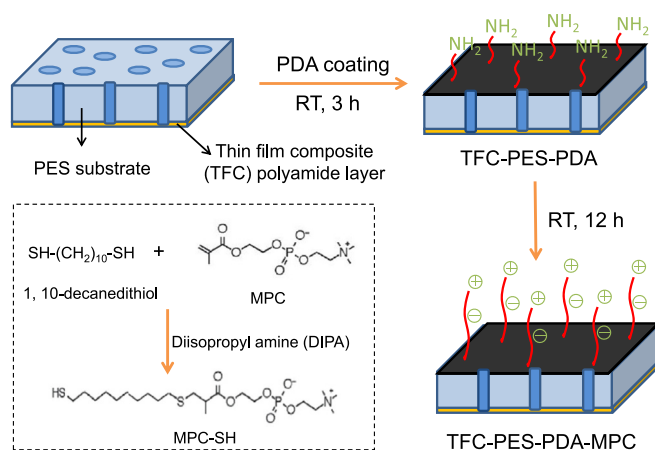


Fig. 1. Illustration of the synthesis of MPC-SH and schematic procedure for the fabrication of TFC-PES-PDA-MPC membranes.

order to facilitate its grafting onto the PES-PDA surface via Michael addition; (3) MPC with a thiol functionality was grafted onto the PES-PDA substrate via Michael addition. It should be noted that MPC-SH has proven to be not cytotoxic to human lung cells in a previous study since the MPC monomer has the same zwitterionic group as phospholipid (Sangsuwan et al., 2016). The high biocompatibility of MPC-SH avoids any secondary contamination to the water source. To the best of our knowledge, TFC-PES membranes grafted by simple but effective zwitterions have not been investigated in the field of osmotic power generation via PRO processes.

2. Materials and methods

2.1. Materials

Diisopropylamine ($\geq 99.5\%$), 2-methacryloyloxyethyl phosphorylcholine (MPC, 97%), dopamine hydrochloride (99%), triethylamine ($\geq 99\%$), tris(hydroxymethyl)aminomethane (tris, $\geq 99.8\%$) and fluorescein isothiocyanate conjugated bovine serum albumin (BSA-FITC) were all purchased from Sigma-Aldrich and used as received without further purification. 1, 10-decanedithiol (HS-C10-SH) was obtained from TCI (Tokyo, Japan). Gram-negative *Escherichia coli* (*E. coli*, ATCC DH5 α) and Gram-positive *Staphylococcus aureus* (*S. aureus*, ATCC 25923) were from American Type Culture Collection, Manassas, VA, USA.

2.2. Synthesis of thiolated-2-methacryloyloxyethyl phosphorylcholine (MPC-SH)

MPC-SH was synthesized by a previously reported method (Goda et al., 2013; Sangsuwan et al., 2016). Briefly, MPC (1.48 g, 5 mmol) and 1, 10-decanedithiol (HS-C10-SH) (2.06 g, 10 mmol) were dissolved in 20 ml degassed chloroform. Diisopropylamine (27.9 μ L, 0.2 mmol) was then added to the mixture solution. After stirring for 20 h at room temperature, the solution was precipitated into acetone. The solid product collected was dried and dissolved in water. MPC-SH was obtained as white powder after freeze-drying.

2.3. Preparation of TFC-PES-PDA-MPC hollow fiber membranes

The PES hollow fiber substrate was spun from poly (ether sulfone) as previously described (Wan and Chung, 2015; Zhang and Chung, 2013). Then a thin polyamide selective layer was synthesized on its inner surface by interfacial polymerization (Li et al.,

2014; Wan and Chung, 2015; Zhang and Chung, 2013). As shown in Fig. 1, the outer TFC-PES-PDA surface was prepared by coating the TFC-PES membrane with a tris buffer solution (10 mmol/L, pH 8.5) containing 2 mg/ml dopamine-HCl for 3 h. The TFC-PES-PDA-MPC membrane was obtained by further coating the outer surface of TFC-PES-PDA with a 1 mg/ml MPC-SH solution with trimethylamine of 1% (v/v) at room temperature for 12 h. The prepared hollow fiber membrane was immersed in DI water for further tests.

2.4. Characterization of hollow fiber membranes

X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Kratos AXIS Ultra DLD spectrometer with a monochromatized Al K α X-ray source (1486.71 eV photons). Both wide scan and core-level spectra were determined. The core-level signals were obtained at the photoelectron take-off angle (α , with respect to the sample surface) of 90°. Binding energy peaks were all calibrated with reference of neutral C 1s hydrocarbon peak at 284.6 eV. The morphology of hollow fiber membranes was investigated by a field emission scanning electronic microscope (FESEM, JEOL JSM-6700F). Before FESEM tests, the samples were freeze-dried and prepared in liquid nitrogen, followed by platinum sputtering.

2.5. Protein adsorption and bacteria adhesion tests

Antifouling efficiency of PES-PDA-MPC was investigated by both protein adsorption and bacteria adhesion tests. The protein adsorption test was performed with fluorescein isothiocyanate conjugated bovine serum albumin (BSA-FITC). The hollow fiber membranes were rinsed with phosphate buffered saline (PBS, 10 Mm, pH 7.4), and subsequently immersed in the BSA-FITC solution (0.5 mg/ml in PBS) at 37 °C for 2 h. After the membranes were washed with PBS, a Leica DMLM fluorescence microscope (Leica Microsystems, Wetzlar, Germany) detected the adsorption of BSA-FITC on the membrane surfaces with an excitation filter of 495 nm and an emission filter of 525 nm.

Both Gram-negative *E. coli* and Gram-positive *S. aureus* were cultured to study the antibacterial adhesion performance of zwitterion modified hollow fiber membranes. First, the bacteria which grew in the tryptic soy broth for overnight were suspended in PBS at a concentration of 5×10^7 cells/ml. Then the hollow fiber membranes were soaked in the bacteria solution at 37 °C for 4 h, after which the membranes were rinsed with PBS for three times to remove loosely and free bacteria from the membrane surface. Spread plates were carried out to quantify and compare the bacteria attachment and viability. The bacteria-adhered membranes were washed in 2 ml of sterile PBS under mild ultrasonication for 7 min. Then a rapid vortex mixing for 1 min was applied. A 100 μ L aliquot was spread onto the solid agar plate containing the culture media. The bacteria were subsequently incubated at 37 °C for 12 h, after which the number of bacteria colonies was counted. The relative viability of bacteria compared to the unmodified TFC-PES membranes was presented. To qualitatively analyze the bacteria adhesion, after rinsed with PBS, the adhered bacteria were fixed with 3% (v/v) aqueous glutaraldehyde at 4 °C overnight. Then the membranes were serially dehydrated in 20, 40, 60, 80, and 100% of ethanol for 10 min each. After drying under a reduced pressure, the membranes were sputter-coated with a thin layer of platinum and scanned by FESEM.

2.6. Membrane fouling tests in PRO processes

PRO fouling tests were conducted on a laboratory-scale PRO setup with synthetic seawater brine (0.81 mol/L NaCl) as the draw solution and wastewater from municipal recycle plants as the feed

solution. The selective layer of the membrane was facing the draw solution in all the tests. The draw and feed solutions flowed counter-currently in the lumen and shell sides, respectively. The flow rate of the two solutions was 0.2 L/min and the temperature was kept at room temperature of 25 °C. Before any data was recorded, the membranes were first stabilized at 15.0 ± 0.5 bar for 0.5 h. An initial water flux with DI water as the feed solution was also measured under the same conditions. After recording the weight decline of the feed solution for each 3 h, backwash was carried out by feeding deionized water into the lumen side at 15.0 ± 0.5 bar for 0.5 h while rinsing the shell side with deionized water without any hydraulic pressure applied. Water flux (J_w , L m $^{-2}$ h $^{-1}$, abbreviated as LMH) is calculated from the weight decline of the feed solution during a certain duration using Eq. (1):

$$J_w = \Delta m / (A \cdot \Delta t \times 1000) \quad (1)$$

where Δm (g) is the mass of water permeated across the effective membrane area A (m 2) over a time period of Δt (h), assuming the density of water is 1000 g L $^{-1}$.

The power density is calculated by Eq. (2):

$$W = J_w \cdot \Delta P \quad (2)$$

where ΔP is the hydraulic pressure difference across the membrane and J_w is the water flux.

3. Results and discussion

3.1. Membrane characterization

The outer surface morphology of PES, PES-PDA, and PES-PDA-MPC substrate layers was investigated by FESEM. As shown in Fig. 2, before modification, the PES substrate is highly porous. It becomes smoother and less porous after the polydopamine coating. However, after the MPC-SH coating, the outer surface becomes porous again. This might be attributed to the fact that some short polyamide chains or non-reacted functional groups of the PDA coating have been attacked by the alkaline environment during the MPC-SH coating. As the molecular size of MPC-SH is not very large, the coating did not cause apparent changes in surface morphology from the cross-section view, indicating the modification has no visible effects on the membrane structure.

However, the successful coatings of PDA and MPC-SH can be verified by XPS. Fig. 3 shows both the wide scan and core-level spectra of the outer porous surfaces of PES, PES-PDA, and PES-PDA-MPC substrates. The pristine PES substrate exhibits C 1s, O 1s, as well as small concentrations of S 2s and S 2P from sulfur. The high energy resolution spectrum of C 1s splits into three groups including C–H/C–C, C–O/C–SO $_2$ and π - π^* groups. After the PDA treatment, a nitrogen peak in the wide scan spectrum is observed which indicates the successful coating of PDA, whereas the peaks of sulfur disappear as the surface of PES is fully covered by the PDA coating. The C 1s core-level spectrum of PDA layer can be curve-fitted into five peaks with binding energies at about 284.6, 285.7, 286.2, 287.5 and 288.3 eV due to respective C–N, C–H, C–O, C=O, and O–C=O functional groups which are all components of PDA. In the case of PES-PDA-MPC, the presence of phosphor peaks in the high energy resolution spectrum of P 2p, with binding energies at about 132.7 and 133.6 eV, is the direct evidence of the MPC coating on the outer surface of modified membranes. The [N]/[P] ratio of PES-PDA-MPC membrane is about 13:1. As MPC-SH has a theoretically equal number of N and P atoms, the extra nitrogen atoms on the surface of the PES-PDA-MPC membrane should be attributed to the PDA layer due to the partial coverage of the MPC layer.

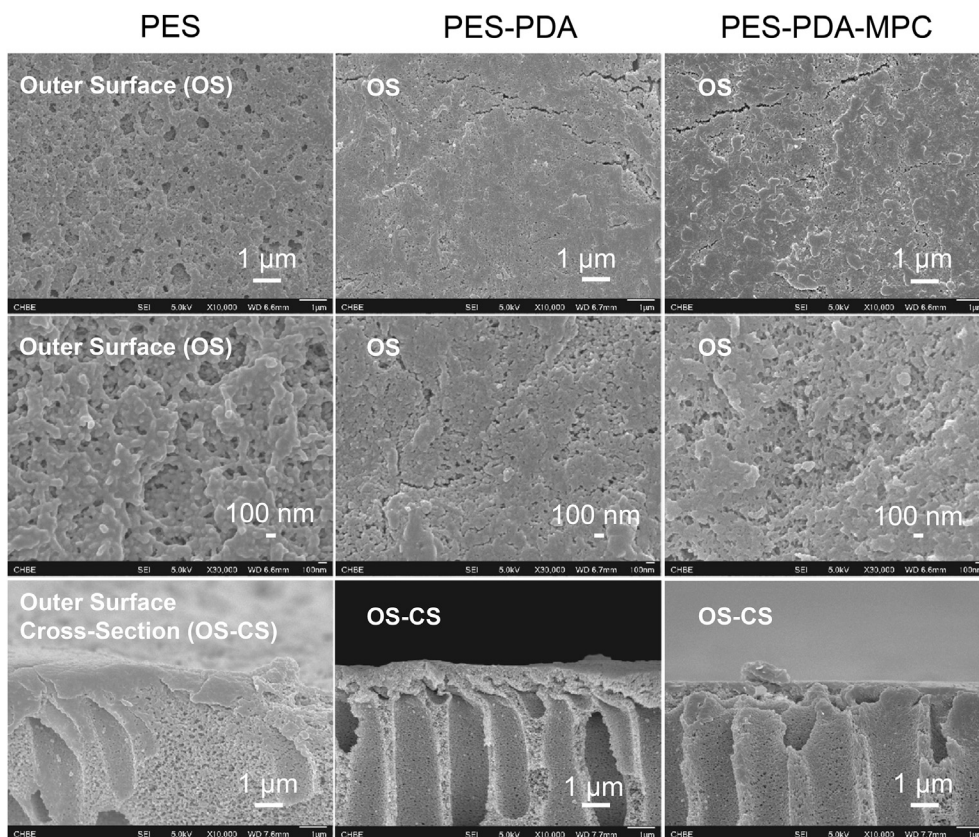


Fig. 2. Comparison of outer surface and cross section of PES, PES-PDA and PES-PDA-MPC hollow fiber substrates.

3.2. Protein adsorption and bacteria adhesion test

The antifouling properties of a membrane can be directly correlated to its resistance against protein and bacteria adsorption (Cai et al., 2016; Lei and Ulbricht, 2014; Li et al., 2014, 2016; Escobar and Van der Bruggen, 2011). In this work, protein adsorption was investigated by measuring the relative fluorescence intensity of membranes treated by a fluorescein isothiocyanate conjugated bovine serum albumin (BSA-FITC) solution. Fig. 4 presents the fluorescence microscopy images and relative fluorescence intensities on the outer surfaces of PES, PES-PDA, and PES-PDA-MPC substrates. Due to the hydrophobic interaction between the protein molecules and conjugated benzene rings of PES, the pristine PES substrate has been covered with the highest amount of BSA-FITC. The protein adsorption on the PES-PDA substrate is reduced which may arise from the smoother surface and also the repulsive force after the PDA coating (Dreyer et al., 2012; Liebscher et al., 2013). The fluorescence intensity further drops to 31.0% after the MPC coating because of the enhanced hydrophilicity and unique zwitterionic properties against fouling.

Bacteria adhesion tests were also conducted with Gram-negative *E. coli* and Gram-positive *S. aureus*. As illustrated in Fig. 5, the pristine PES substrate is seriously fouled by both *E. coli* and *S. aureus* in 4 h. As substrate pores are larger than the bacteria size, the bacteria not only adhere to the surface, but also penetrate into the membrane pores. After the polydopamine coating, the *E. coli* and *S. aureus* attachments are still remarkably high. The difference in the adhesion of *E. coli* and *S. aureus* on the PES-PDA is caused by the charge difference. *E. coli* is a type of gram-negative bacteria while *S. aureus* is a type of gram-positive bacteria. Since polydopamine (PDA) is negatively charged, *S. aureus* is more likely

to adhere to the PES-PDA surface because of their electrostatic interactions. Compared to the PES and PES-PDA substrates, the substrate surface of PES-PDA-MPC has a significant reduction in both *E. coli* and *S. aureus* adhesion. To quantitatively determine the difference in viable bacterial adhesion, spread plates were performed. Fig. 5 (a) summarizes the results which are in accordance with FESEM analyses, as shown in Fig. 5 (b). Comparing to the pristine PES substrate, PES-PDA-MPC reduces the *E. coli* and *S. aureus* adhesion to 8.7% and 26.3%, respectively. Therefore, the zwitterionic coating is effective in reducing bacteria adhesion onto the membrane surface and pores.

There are two primary reasons for the antifouling properties of MPC coated PES membranes. Firstly, the cationic and anionic groups of MPC result in net electrical neutrality. This would diminish the electrostatic interactions between the membrane surface and foulants in the feed solution. On the other hand, the surface coating by zwitterions increases the hydrophilicity of the membrane surface (Yu et al., 2014; Zheng et al., 2016). Thus, a strong hydration layer above the MPC coating is formed due to the zwitterions of MPC. This hydration layer would shield the membrane surface and prevent foulants from contacting the membrane surface (Cai et al., 2016; Goda et al., 2013; Razi et al., 2012; Sangsuwan et al., 2016; Schlenoff, 2014).

3.3. Antifouling performance in PRO processes

The PRO tests were all performed at 15 ± 0.5 bar for the TFC-PES, TFC-PES-PDA and TFC-PES-PDA-MPC membranes. Fig. 6 shows the normalized PRO water flux (i.e., normalizing it to the initial water flux with deionized water as the feed solution) of pristine TFC-PES and TFC-PES-PDA-MPC hollow fiber membranes in PRO tests. The

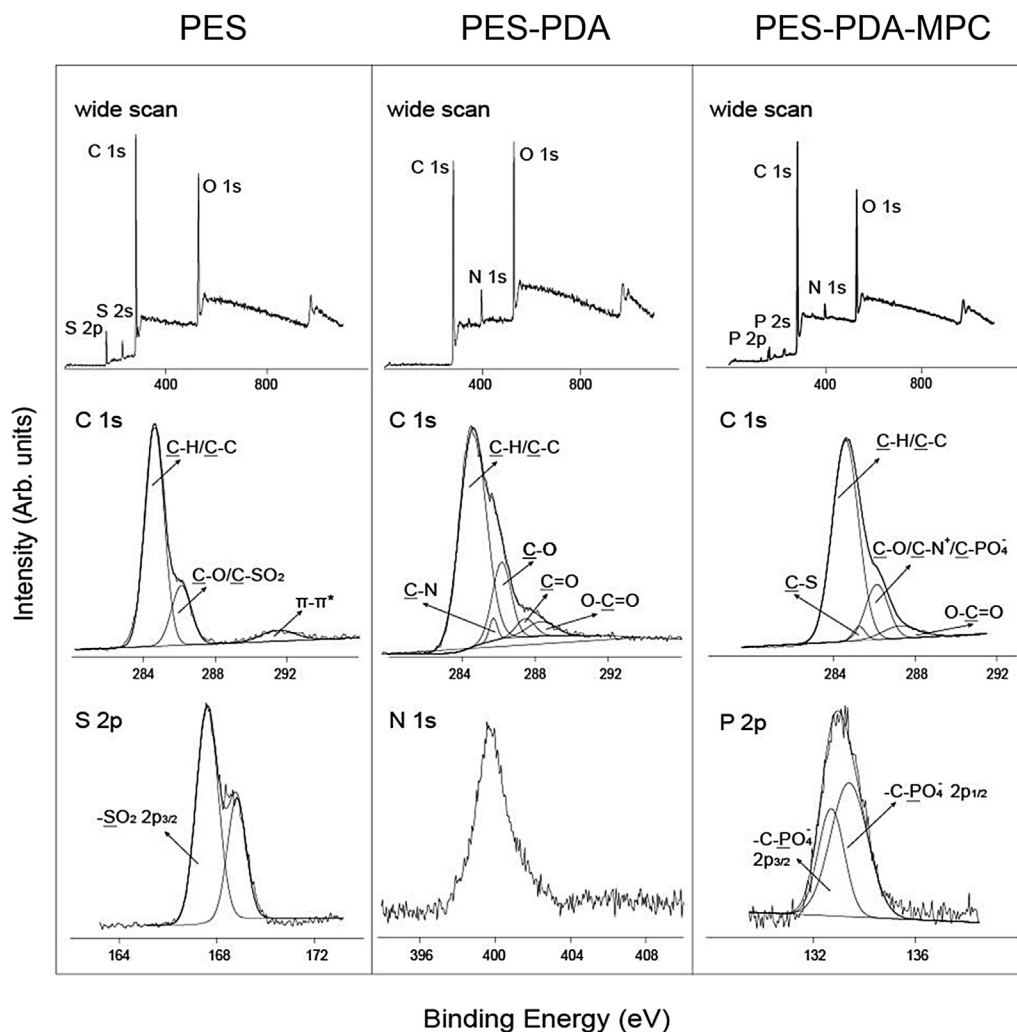


Fig. 3. XPS wide scan, C 1s, N 1s, P, 2p and S 2p core-level spectra of PES, PES-PDA and PES-PDA-MPC hollow fiber substrates.

feed solution in this work was a retentate from a municipal wastewater plant which contained a wide range of impurities. The detailed composition of the wastewater has been reported in previous study (Chen et al., 2015, 2016; Wan and Chung, 2015).

For the pristine TFC-PES membranes, when the wastewater was fed as the feed solution, the water flux dropped to 82.1% of the initial water flux within the first 5 min. Then it gradually declined to about 55% at 50 min. At the end of the 1st run, the total reduction in water flux was 48% for the pristine TFC-PES membranes. The fast decline in the water flux indicates the high affinity to fouling of unmodified PES substrates caused by the wastewater. In comparison, the water flux of modified membranes, TFC-PES-PDA-MPC, reduced much less rapidly over the first 40 min. Subsequently, the water flux stayed stable in a small range of 68–75% of the initial water flux. The power density of TFC-PES-PDA-MPC membranes at the end of the 1st run was 7.7 W/m², which is about 30% higher than that of pristine TFC-PES membranes.

After each 3 h's operation, back washing at 15 ± 0.5 bar on the draw solution side for 30 min was carried out with deionized water fed onto the both sides of hollow fiber membranes. The recovery rate of water flux could be higher than 86%. In the following runs of PRO under the same operation conditions, the TFC-PES-PDA-MPC membranes still showed a higher resistance to foulants in the wastewater feed. In the end of 3 runs, the modified membranes

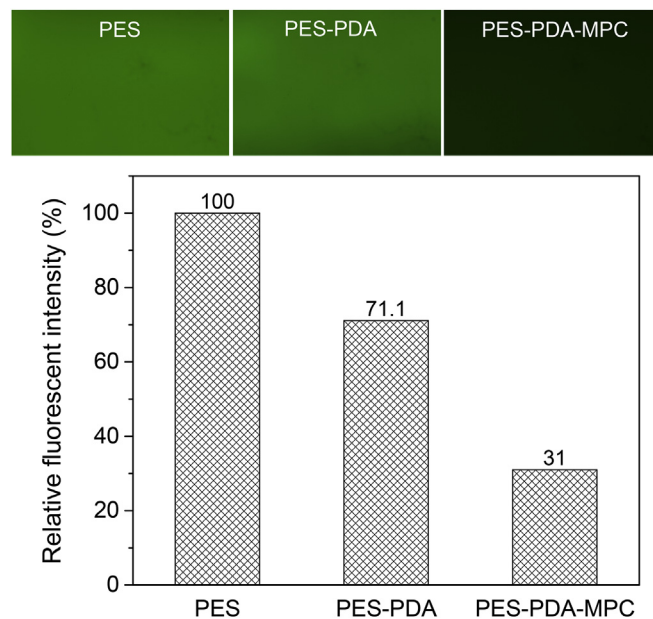


Fig. 4. Fluorescence microscopy images and relative fluorescence intensities of the support layer surfaces of the PES, PES-PDA and PES-PDA-MPC hollow fiber substrates after exposure to a 0.5 mg/ml BSA-FITC solution for 2 h.

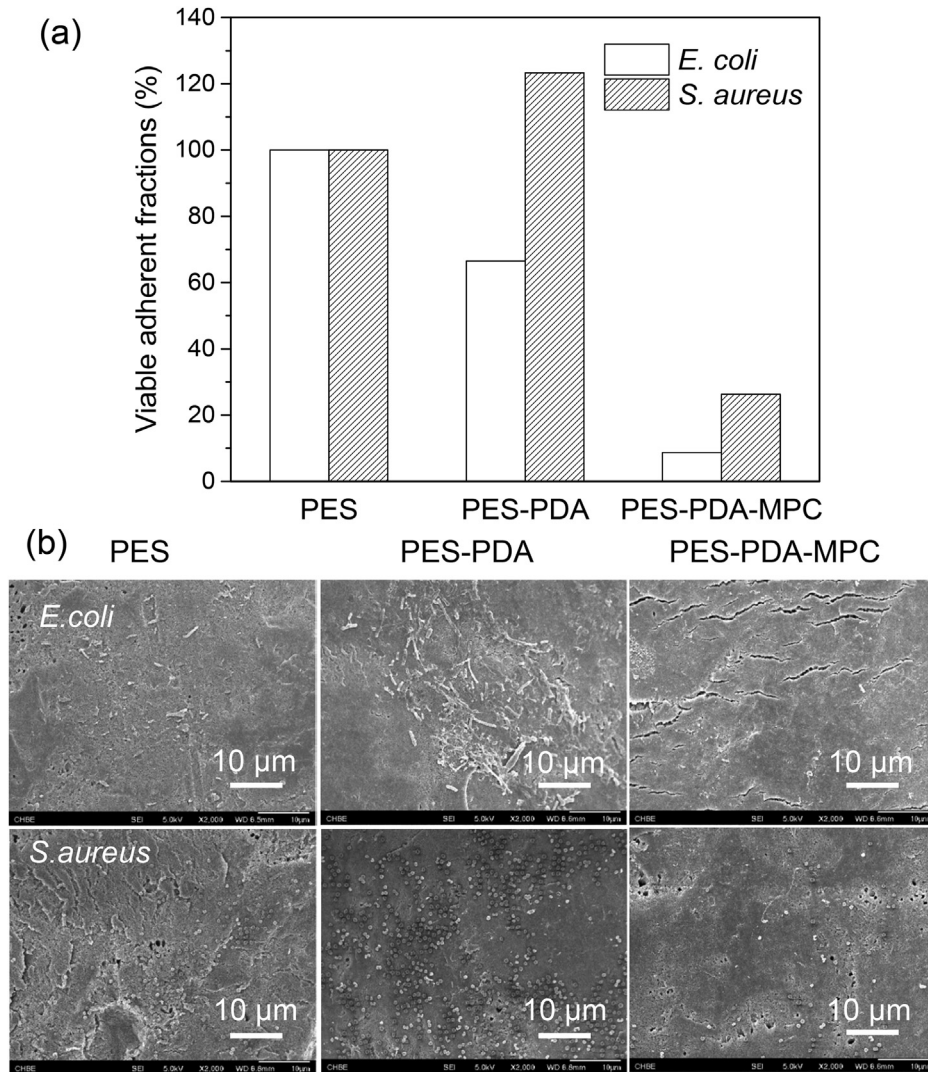


Fig. 5. (a) Viable adherent fraction of cells on PES, PES-PDA and PES-PDA-MPC hollow fibers after exposure to *E. coli* and *S. aureus* at an initial cell concentration of 5×10^7 cells/ml for 4 h at 37 °C; (b) FESEM images of outer surfaces of PES, PES-PDA and PES-PDA-MPC after bacteria exposure.

exhibited 50% higher power density than the unmodified ones. As listed in Table 1, the average power density generated by TFC-PES-PDA-MPC in the 3 runs was 7.2 W/m^2 , while it was 4.8 W/m^2 for the unmodified TFC-PES membranes. Therefore, the MPC coated TFC-PES membranes not only exhibit higher antifouling efficiency but also show high potential for osmotic power generation via PRO processes.

4. Conclusions

In this work, we have designed and fabricated the zwitterions coated TFC-PES hollow fiber membranes with enhanced antifouling properties for osmotic power generation via PRO processes. XPS analyses confirm the success of MPC coating on the outer surface of PES substrates. The coating of zwitterion layer provides good resistance to both protein adsorption and bacteria attachment which is proved by the protein adsorption and bacteria adhesion tests with BSA, *E. coli* and *S. aureus* as the foulants. In the PRO antifouling tests under 15 bar, the modified TFC-PES membranes achieved much better performance in terms of water flux and power density compared to the unmodified ones. After 3 runs of PRO

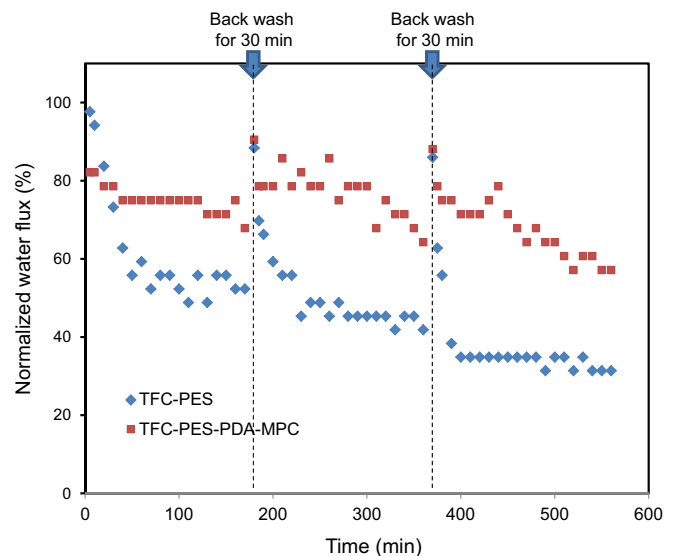


Fig. 6. PRO fouling performance of TFC-PES and TFC-PES-PDA-MPC membranes using municipal wastewater as the feed.

Table 1

Summary of the salt rejection and power density of the PES and PES-PDA-MPC hollow fiber membranes.

Membrane	Salt flux (gMH)	Power density (W/m ²)				Average
		Initial	After 1st run	After 2nd run	After 3rd run	
TFC-PES	66.9	11.5	6.0	4.8	3.6	4.8
TFC-PES-PDA-MPC	62.1	11.3	7.7	7.3	6.5	7.2

processes, the reduction in power density of TFC-PES-PDA-MPC is about 16%, while it is about 40% for the pristine ones. This work may provide a useful approach for the fabrication of antifouling PRO membranes to facilitate the employment of municipal wastewater as the feed solution in PRO processes.

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