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### 1. Introduction

Pressure retarded osmosis (PRO) has provided intensive impetus to the exploration and development of high performance membranes for converting clean and sustainable osmotic power into electricity.<sup>1-11</sup> Preliminary experiments demonstrated that the replacement of deionized (DI) water with wastewater retentates resulted in the sharp decline of power density from a maximum of ~27 W m<sup>-2</sup> to 0 W m<sup>-2</sup> after a short operation period.<sup>12-16</sup> Although pretreatment processes on feed solutions brought about some improvements, the accumulation of contaminants within the porous support and vulnerable coating inevitably caused severe internal concentration polarization and bacterial biofilm formation in long term operations.

## Hyperbranched poly(ionic liquid) functionalized poly(ether sulfone) membranes as healable antifouling coatings for osmotic power generation<sup>†</sup>

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Membrane fouling and membrane deterioration are two major concerns since they greatly worsen membrane performance in pressure retarded osmosis (PRO) and shorten the membrane lifetime. Herein, inspired by biological systems where microdamage induces an autonomous repair process, intrinsically healable poly(ionic liquid) (PIL) coating layers with sufficiently high mobility from short-distance electrostatic interactions have been fabricated by sequential immobilization of sulfonated hyperbranched polyglycerol (hbSPG) and guaternized polyethylenimine (QPEI) on polydopamine (PDA) pretreated poly(ether sulfone) (PES) membranes. XPS, SEM, and AFM results confirmed the successful incorporation of a PIL polymer pair onto the PES supports. Zeta potential analysis validated the charge alteration by electrostatic conjugation of the QPEI polymer onto the hbSPG modified surface. The antifouling and self-healing characteristics of the resultant PES-g-hbSPG-QPEI hollow fiber membranes were demonstrated by the excellent anti-protein adsorption behaviors and improved antibacterial performances on both non-aged and aged samples that were soaked in real municipal wastewater (WWRe) for two months. In PRO tests, the pristine PES membranes were contaminated seriously under high pressure operation, leading to a significant flux drop of 60%. In comparison, a flux reduction of 30% and a recovery rate of 98% after backflushing and hydraulic pressure impulsion on the non-aged membrane and a flux reduction of 40% on the aged membranes were observed. The intrinsically healable and antifouling PIL coating layers exhibit great potential of the developed strategy for the fabrication of high-performance PRO membranes toward osmotic power generation.

The impurities would readily be stuck in the porous membrane matrix rather than the dense selective layer, and thereby aggravate the fouling behavior.<sup>17–22</sup> In an effort to boost the power density of the PRO process, the establishment of multi-layer coating structures with superior fouling resistance, self-healing characteristics and high osmotic pressure toleration on the membranes is of great significance.

Most coating layers are soft and susceptible to mechanical damage especially for membranes under great pressure in practical usage. Continuous attacks and corrosion by inorganic substances, organic compounds and microorganisms in feed solutions result in occasional scratches or partial exfoliation on the coating layers and thereby disclose the underlying membrane matrix. With regard to the antifouling coating layers, myriad metabolic substances including corrosive ammonia and organic acids excreted by the attached bacteria during their reproductive processes further destroy the already defective coating layers and eventually deprive them of their protective functions.23-25 Inspired by biological systems where microdamage triggered an autonomous repair process with minimum external intervention, self-healing materials with diverse dynamic bond connections have been developed.<sup>26-31</sup> Current self-healing behavior mainly focuses on bulk materials

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like hydrogels that are capable of restoring their mechanical and structural integrity. It has been gradually applied to surface coatings to sustain preliminarily incorporated functions, such as antifouling and anticorrosive performances. Differing from conventional coatings, self-healing coatings capable of detecting internal defects within the coatings and autonomously repairing themselves to recover their original functions are acknowledged as a promising strategy to address the increasing sophisticated fouling problems and are of crucial necessity to reduce maintenance costs, extend service lifespan and enhance reliability of the underlying membranes.

Poly(ionic liquid)s (PILs) are an emerging and intriguing subclass of functional polymers with repeating units that bear ionic liquid (IL) moieties.<sup>32,33</sup> The structural synergy between the IL component and the macromolecular architecture broadens the window of physicochemical properties of common polyelectrolytes and thereby enriches their function and application spectrum by combining the beneficial characteristics from ILs, such as high ionic conductivity, remarkable chemical, electrochemical and thermal stability, structural variability and strong polarizability, with the intrinsic polymer features including superior processability and spatial tunability.<sup>34-37</sup> Although there are many self-healing paradigms in nature, it is still greatly challenging to transform them into engineering materials. Moreover, in self-healing coatings, the confined mobility of the polymer brushes within the nanoscale thickness has hitherto restricted the self-recovery behavior upon mechanical damage because the reversible interaction can be rebuilt only when the polymers can migrate across the damaged area and come into intimate contact with each other. In this contribution, upon establishing the role of PILs in membrane modification, intrinsically healable PIL coating layers with sufficiently high mobility from short-distance electrostatic interactions, have been constructed by the sequential conjugation of sulfonated hyperbranched polyglycerol (hbSPG) and quaternized polyethylenimine (QPEI) on polydopamine (PDA) pretreated membrane supports. To the best of our knowledge, the current work is the first example on the preparation of PILbased PRO membranes with self-healing characteristics and fouling resistant features for osmotic power generation.

### 2. Experimental section

#### 2.1 Materials

Dopamine hydrochloride (DA, 99%), tris(hydroxymethyl)aminomethane (Tris,  $\geq$ 99.8%), triethylamine (TEA,  $\geq$ 99%), copper(II) sulfate (CuSO<sub>4</sub>,  $\geq$ 99%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 wt%) and poly(diallyldimethylammonium chloride) solution (PDDA,  $M_w < 100\ 000$ , 35 wt%) were purchased from Sigma-Aldrich and used as received except where mentioned otherwise. Sulfonated hyperbranched polyglycerol (hbSPG,  $M_{n,NMR} = 12\ 200\ g\ mol^{-1}$ ,  $M_{n,GPC} = 9800\ g\ mol^{-1}$ , D = 1.22),<sup>38-41</sup> quaternized poly(ethylenimine) (QPEI, linear,  $M_{n,GPC} = 18\ 000\ g\ mol^{-1}$ , D = 1.24)<sup>42,43</sup> and PES-TFC dual-layer hollow fiber supports were prepared according to the protocols reported in the literature.

#### 2.2 Preparation of the PES-g-hbSPG-QPEI or PES-g-hbSPG-PDDA hollow fiber membranes

As shown in Scheme 1, the construction of sandwiched multilayer coatings on the PES-TFC dual-layer hollow fiber substrates was carried out in three successive steps. A Tris buffer solution  $(0.05 \text{ mol } L^{-1}, \text{ pH } 8.5)$  containing DA (2.0 mg mL<sup>-1</sup>), CuSO<sub>4</sub>  $(0.85 \text{ mg mL}^{-1})$  and  $H_2O_2$   $(0.9 \text{ mg mL}^{-1})$  was preliminarily dosed to the shell channel of the PES-TFC hollow fiber membranes at ambient temperature for 3 h to provide adequate reaction sites for the subsequent polymer grafting. The pretreated membranes, denoted as PES-PDA membranes, were washed with deionized (DI) water for 0.5 h. Afterward, the polydopamine coating solution was replaced by a hbSPG solution  $(10 \text{ g L}^{-1})$  containing TEA  $(0.1 \text{ mol L}^{-1})$  and the Michael addition reaction was allowed to proceed for 12 h. After that, the intermediate membranes, denoted as PES-g-hbSPG membranes, were rinsed with DI water for an additional 0.5 h. For the second polyelectrolyte layer, a diluted QPEI or PDDA solution (10 g  $L^{-1}$ ) was dosed to the shell channel of the membranes for another 12 h. The resultant membranes, denoted as PES-g-hbSPG-QPEI or PES-g-hbSPG-PDDA membranes, were then extracted thoroughly and stored in DI water to eliminate any leftover polymers before further tests.

#### 2.3 Characterization

X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos AXIS Ultra DLD spectrometer with an Al Ka X-ray source to investigate the surface chemistry evolution of the membranes. A field emission scanning electronic microscope (FESEM, JEOL JSM-6700F) was employed to observe the surface morphologies of the resultant membranes. The membrane specimens were initially cut in liquid nitrogen for sharp crosssections and then platinum-coated by a JEOL JFC-1100e Ion Sputtering device prior to FESEM observation. The surface charge profiles of the modified membranes were evaluated via a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). PES flat sheet membranes were prepared using a similar method to simulate the outer surface charge properties of the hollow fiber membranes. The flat sheet membrane sample was first placed in a 0.01 mol  $L^{-1}$  NaCl solution of pH 2.5. During measurement, the NaCl solution was slowly auto-titrated with 0.05 mol  $L^{-1}$  NaOH to pH 10. The  $\zeta$ -potential of the membrane surface was then measured against the elevated pH values.

Fluorescein isothiocyanate conjugated bovine serum albumin (BSA-FITC) and  $\gamma$ -globulin ( $\gamma$ -globulin-FITC) were adopted in the protein adsorption experiments. The membrane specimens were initially cut to 2 cm in length and positioned in isotonic phosphate buffered saline (PBS, 0.01 mol L<sup>-1</sup>, pH 7.4) containing BSA-FITC or  $\gamma$ -globulin-FITC (1.0 mg mL<sup>-1</sup>) at 37 °C for 2 h. The relative fluorescence intensity of the surface-bound protein amount after being thoroughly rinsed with PBS was quantified using a Leica DMLM fluorescence microscope (Leica Microsystems, Wetzlar, Germany).

Two bacterial strains including *E. coli* (ATCC 25922) and *S. aureus* (ATCC 25923) were cultivated to investigate the antimicrobial behavior of the poly(ionic liquid) conjugated



Scheme 1 Schematic of the procedure for the fabrication of PES-g-hbSPG-QPEI membranes.

membranes. The bacterial suspension was fixed at  $1 \times 10^8$  colony forming unit (CFU) per mL by diluting overnight cultured bacteria with sterile PBS. The membrane samples of 2 cm length were positioned in a sterile plastic tube with 10 mL bacterial suspension. The tube was incubated in a shaking bed at 100 rpm at 37 °C for 6 h. The samples were then removed and gently rinsed thrice with PBS to eliminate the unattached or dead bacterial cells. Qualitative analyses of the contaminated membranes were directly performed by FESEM observation while quantitative measurements were obtained by the spread plate method with each result reported from the mean value over at least five concurrent samples.

#### 2.4 Membrane fouling assays in PRO processes

The fouling tests against WWRe were performed in a lab-scale PRO setup as demonstrated in Scheme S1,† feeding 3 L synthetic SWBr (0.81 mol  $L^{-1}$  NaCl) in the draw side and 1 L WWRe in the feed side. The WWRe has total dissolved solids (TDS) in the range of 1000-1350 ppm, of which the major cations are Na<sup>+</sup> (13–17%) and Ca<sup>2+</sup> (8–10%) and the major anions are  $SO_4^{2-}$  (22–25%) and  $Cl^-$  (14–17%). Its biochemical oxygen demand (BOD) is in the range of 3-10 ppm, and its chemical oxygen demand (COD) is in the range of 150-220 ppm. Touati and Tadeo reported that reverse salt diffusion and produced power are affected by the operating conditions.<sup>44</sup> The operating conditions have been optimized in our previous studies45,46 and therefore the operating pressure was maintained at 15  $\pm$  0.2 bar at the draw side during each 10 h testing cycle. To provide high velocity, equal flow rates of 0.2 L min<sup>-1</sup> were maintained for both the feed and draw sides without any concentration/temperature adjustments to both the solutions throughout the whole test period. The membranes were subjected to pressure-conditioning at 15 bar for 0.5 h before each testing run, where DI water was dosed to the feed solution. In between each fouling test run, DI water was fed into the lumen side of the membranes to backflush the fouled membrane at a transmembrane pressure ( $\Delta p$ ) to facilitate the removal of the contaminants. The water permeation flux in this process,  $J_w$ (L m<sup>-2</sup> h<sup>-1</sup>), can be deduced from the following relation:

$$J_{\rm w} = \Delta m / (A \Delta t \rho)$$

where  $\Delta m$  (g) denotes the mass of water transported across the effective membrane area A (m<sup>2</sup>) at predetermined time intervals  $\Delta t$  (h) and  $\rho$  denotes the density of water (g L<sup>-1</sup>). The normalized water flux is calculated *via*  $J_w/J_i$ , where  $J_i$  is the initial water permeation flux during the first 10 min. In parallel assays, the modified membranes were aged by immersion in WWRe for two months to further assess the antifouling and self-healing characteristics of the PIL coating layers. For each membrane module, the effective membrane area was 11.2 cm<sup>2</sup>.

### 3. Results and discussion

#### 3.1 Preparation of the poly(ionic liquid) functionalized PESg-hbSPG-QPEI or PES-g-hbSPG-PDDA hollow fiber membranes

Mussel-inspired polydopamine (PDA) coatings have been widely implemented in various membrane separation techniques as they enable a reversible or irreversible bridge between the inert inorganic or organic surface and diverse functional polymers *via* Schiff base or Michael additions.<sup>47-49</sup> Ingole *et al.* investigated the effect of the PDA coating on PRO membranes and achieved an increase in the power density for the PDA-TFC membranes.<sup>50</sup> Oxidative self-polymerization of dopamine by using air as an exclusive oxidant, which usually proceeds randomly on the membrane surface, enabled the generation of a deficient amount of irregular PDA nanoparticles and incomplete coverage of the surface in a sluggish growth fashion. In consideration of the reduced selectivity and permeability arising from the inappropriate coating strategies especially in the increasingly sophisticated membrane separation systems, a stronger and stable CuSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> oxidant stood out as a promising candidate, leading to the continuous deposition of small and uniform PDA nanoparticles on the membrane surface with negligible structural defects, tunable thickness and favorable polymerization kinetics.51 It also enabled large-scale membrane functionalization with consistent performance and feasibility at low industrial cost. In the present study, compact coverage of the PDA gutter layer with thickness over 10 nm was formed by dosing the Tris buffer solution with dopamine and CuSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> oxidant to the shell channel of the PES-TFC membranes for 3 h, as elucidated by the signal screening of the underlying S element and a [N]/[C] ratio of approximately 0.11 in the X-ray photoelectron spectroscopy (XPS) wide-scan spectrum (Fig. S1a and S1d<sup>†</sup>). The deconvoluted C 1s corelevel spectrum split into five peaks, with the respective binding energies (BEs) at 284.6 eV for the -CH-/-C-C species, 285.6 eV for the -C-N species, 286.2 eV for the -C-O species, 287.4 eV for the -C=O species and 288.8 eV for the O-C=O species, which is in good correlation with the chemical structure of neat PDA (Fig. S1e<sup>+</sup>).<sup>40,52,53</sup>

As macromolecular precursors for the fabrication of poly-(ionic liquid) (PIL) coatings, sulfonated hyperbranched polyglycerol (hbSPG,  $M_{n,NMR} = 12\ 200\ g\ mol^{-1}$ ,  $M_{n,GPC} = 9800\ g\ mol^{-1}$ , D = 1.22, Scheme S2†) was preliminarily produced by the anionic ring-opening multi-branching polymerization of glycidol, followed by sulfonation of the hydroxyl groups with sulfamic acid whereas quaternized poly(ethylenimine) (QPEI, linear,  $M_{n,GPC} =$ 18 000 g mol<sup>-1</sup>, D = 1.24) was synthesized by the partial hydrolysis of commercial poly(2-ethyl-2-oxazoline) ( $M_{n,GPC} = 25\ 000\ \mathrm{g\ mol}^{-1}, D < 1.4$ ), followed by quaternization with methyl iodide. Detailed information about the synthesis and characterization of hbSPG and QPEI is presented in our previous publication and in the ESI (Fig. S2 and S3<sup>+</sup>).<sup>38-43</sup> For comparison purpose, commercial poly(diallyldimethylammonium chloride) (PDDA,  $M_w < 100\ 000$ , 35 wt%) was also employed for the fabrication of PIL coatings.

The construction procedure for the hierarchically structured PIL layer consisted of the successive conjugation of anionic and cationic polyelectrolytes from the PDA gutter layer under mild conditions. hbSPG possesses many outstanding characteristics of dendrimers including tunable molecular weight, narrow dispersity, abundant end-functionalities, high water solubility, thermal stability, chemical resistance and biocompatibility. In addition, it has been widely reported that a branched polymer provides a larger shielding area than its linear counterpart at an equivalent grafting density. XPS wide-scans and C 1s and S 2p core-level spectra of the exterior surface of PES-g-hbSPG membranes were collected and the results are displayed in Fig. 1a, d and e. The signal shielding of the underlying N element and simultaneous signal renascence of S and Na elements in the XPS wide-scan spectrum of the PES-g-hbSPG membrane surface validated the fact that the PDA layer is fully buried under the thick hbSPG branches (Fig. 1a).<sup>39,52,53</sup> The deconvoluted C 1s core-level spectrum comprised four distinctive peaks with BEs at 284.6, 285.6, 286.5 and 288.7 eV, which can be associated with the neutral -CH-/-C-C, -C-S, -C-O/- $\underline{C}$ -SO<sub>3</sub><sup>-</sup> and O- $\underline{C}$ =O species (Fig. 1d), respectively. The deconvoluted S 2p core-level spectrum is composed of two spin-orbit doublets, including the predominant part with BEs at 168.6 and 169.8 eV for the  $-C-\underline{SO}_3^ 2p_{3/2}$  and  $-C-\underline{SO}_3^ 2p_{1/2}$  peak



Fig. 1 XPS wide-scan, C 1s, N 1s and S 2p core-level spectra of the (a, d, and e) PES-g-hbSPG, (b, f, and f') PES-g-hbSPG-QPEI and (c and g) PES-g-hbSPG-PDDA hollow fiber membranes.



Fig. 2 Membrane morphologies of (a1–a4) pristine PES-TFC, (b1–b4) PES-g-hbSPG and (c1–c4) PES-g-hbSPG-QPEI hollow fiber membranes.

components in the hbSPG polymer edges and the rest with BEs at 163.1 and 164.3 eV for the  $-C-\underline{S} 2p_{3/2}$  and  $-C-\underline{S} 2p_{1/2}$  peak components formed by Michael addition (Fig. 1e).<sup>40,52,53</sup>

The combination of a Schiff base complex with residual imine and the PDA gutter layer, and short-distance electrostatic attraction between anionic and cationic polyelectrolytes accounts for the firm binding of QPEI polymers to the membrane surface anchors with high chain mobility and reversible ion-pair interactions.42,43 In self-healing coatings, the confined mobility of the polymer brushes within the nanoscale thickness has hitherto restricted the self-recovery behavior upon mechanical damage because the reversible interaction can be rebuilt only when the polymers can migrate across the damaged area and come into intimate contact with each other. In other words, linear polymers would possess higher mobility than branched polymers and therefore are able to migrate to the edge of the damaged interfaces in close proximity. The degree of neutralization of sulfonate groups in hbSPG was regulated by the feed molar ratio of the corresponding ammonium groups in QPEI in combination with the fast kinetics of the neutralization reaction. The C 1s core-level spectrum can be curve-fitted into two peak components having BEs at 284.6 and 286.5 eV assigned to the -CH-/-C-C and combined -C-O/-C-SO<sub>3</sub><sup>-/-</sup>  $\underline{C}$ -N<sup>+</sup> species, respectively (Fig. 1f). The same result can also be deduced from the complete substitution of the Na element with the N element in the XPS wide-scan spectrum of the PES-ghbSPG-QPEI membranes (Fig. 1b). The N 1s core-level line is occupied by an exclusive peak with a BE at around 402 eV, attributable to the quaternary nitrogen  $(-\underline{N}^{+})$  species from the coupled QPEI (Fig. 1f'). With regard to PES-g-hbSPG-PDDA membranes, similar trends were observed (Fig. 1c and g), except for the increased  $\left[-\underline{C}H-/-\underline{C}-C\right]/\left[-\underline{C}-O/-\underline{C}-SO_{3}^{-}/-\underline{C}-N^{+}\right]$  in correlation with the decreased density of quaternary ammonium groups in PDDA.

# 3.2 Surface chemistry and morphology characterization of membranes

Fig. 2 illustrates the morphologies of the pristine, hbSPG functionalized and PIL coated hollow fiber membranes. All three membranes demonstrate a typical ridge-and-valley polyamide structure on the interior surface. The inner surface (Fig.  $2(a_2)-(c_2)$ ) and cross-section (Fig.  $2(a_1)-(c_1)$ ) of the polyamide layer maintain the same structure with rough ridges, demonstrating that these modification processes cause no



Fig. 3  $\zeta$ -Potential of the PES-*g*-hbSPG and PES-*g*-hbSPG-QPEI membranes as a function of pH.

structural damage to the polyamide selective layer. On the other hand, the outer surface of the three membranes exhibits a porous structure with a relatively smoother surface compared to the polyamide layer. There are many small nodules observed on the outer surface of both PES-g-hbSPG and PES-g-hbSPG-QPEI, indicating the deposition of coating polymers. The AFM results shown in Fig. S4<sup>†</sup> indicate that the pristine PES has the lowest roughness and the polymer grafting amplifies the surface roughness to a small extent, where  $R_{ms}$  increases from 6.9 nm to 9.1 nm. The porous exterior surface of the pristine PES support allows impurities to pass through and accumulate. For PES-g-hbSPG and PES-g-hbSPG-QPEI hollow fiber membranes, dense and rough structures could be wellpreserved and the original surface porous structures are fully covered, elucidating the successful incorporation of the PIL polymer pair onto the PES supports.

The ζ-potential of the PES-g-hbSPG and PES-g-hbSPG-QPEI membranes as a function of pH is exhibited in Fig. 3. In the pH range from 3 to 10, the hbSPG modified membrane is negatively charged, which is mainly attributable to the deprotonation of the ionizable -C-SO<sub>3</sub><sup>-</sup> groups in the hbSPG polyelectrolyte branches. However, after the electrostatic conjugation of the QPEI polymer onto the hbSPG modified surface, the corresponding ζ-potential reverses and becomes positive. The overall membrane charge profiles could be associated with the difference between the positively charged quaternary ammonium groups and negatively charged sulfonate groups. With the increase in the charge density of cationic polymers, a more positive deviation from charge neutrality in the PIL networks was found. The hybrid chelating polymers may provide extra adsorption and repulsion effects for both negatively and positively charged foulants, preventing the foulants from entering into the porous substrates.

### 3.3 Anti-protein and antimicrobial performances of the PES-TFC, PES-g-hbSPG, PES-g-hbSPG-QPEI and PES-g-hbSPG-PDDA hollow fiber membranes

The amount of protein adsorbed on the membrane surfaces is significantly influenced by the ionic strength of the polyelectrolyte pair and the specific features of the ions. In general, anionic polymers tend to bind positively charged proteins ( $\gamma$ globulin, pl = 7.3-8.2) whereas cationic polymers tend to bind negatively charged proteins (BSA, pl = 4.7) via electrostatic attraction to afford different protein build-up on the membrane surfaces.54 To elucidate the effect of surface chemistry evolution on protein adsorption, the involved membranes were placed in two fluorescein labeled protein solutions ( $\gamma$ -globulin-FITC and BSA-FITC). Fluorescence intensities and fluorescence microscopy measurements were recorded for the original PES-TFC and PIL decorated membranes after soaking in 1.0 mg mL<sup>-1</sup> BSA-FITC or γ-globulin-FITC solution for 2 h. The hydrophobichydrophobic interactions among PES and proteins enable the surface to bind a large quantity of proteins. In contrast, the





**Fig. 4** Relative fluorescence intensities of (a) pristine PES, (b) PES-*g*-hbSPG, (c) PES-*g*-hbSPG-QPEI and (d) PES-*g*-hbSPG-PDDA hollow fiber membranes after exposure to 1.0 mg mL<sup>-1</sup> BSA-FITC and  $\gamma$ -globulin-FITC solution for 2 h. Inset pictures are the respective fluorescence microscopy images of protein adsorption on the aged samples.



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**Fig. 6** Viable adherent fractions of (a) pristine PES, (b) PES-*g*-hbSPG, (c) PES-*g*-hbSPG-QPEI and (d) PES-*g*-hbSPG-PDDA hollow fiber supports after exposure to PBS suspensions of *S. aureus* and *E. coli* at an initial cell concentration of  $1 \times 10^8$  CFU mL<sup>-1</sup> for 6 h at 37 °C. The cell number was determined by the spread plate method. Error bars represent the standard deviation of five measurements.

relative fluorescence intensities of BSA and  $\gamma$ -globulin adsorptions significantly reduced to less than 10% on the PIL coated membrane surfaces. The combined results indicated that PIL functionalized membranes can bind various amounts of water and thereby establish a compact surface hydration network that generally exhibits reduced fouling propensity and provides a steric and energetic barrier against the adsorption of hydrophobic impurities (Fig. 4).

A stubborn biofilm forms on the membrane surfaces once the accumulation of bacterial colonies exceeds a certain amount, leading to the decline of membrane permeability, selectivity and lifespan, which is identified as the quorum sensing effect.<sup>25,26</sup> Antimicrobial surface coatings, which could effectively eliminate or neutralize bacteria before they become destructive, are preferable in combating membrane fouling which is acknowledged

as one of the great challenges in membrane separation techniques in water treatment. In the present study, water based assays against two strains, Gram-negative E. coli and Grampositive S. aureus, were adopted to examine the antibacterial behavior of the PIL-coated membranes. A myriad of live bacterial clusters with smooth and unperturbed features were observed on the domestic PES-TFC membranes when contaminated by PBS suspensions of S. aureus and E. coli for a prolonged incubation time of 6 h, with the former exhibiting stronger biofilm formation capability (Fig. 5).40 After surface tethering of hbSPG branches with abundant sulfonate groups that could resist the fouling of hydrophobic bacterial cells, the PES-g-hbSPG hollow fiber membranes became less prone to bacterial attachment, with the respective viabilities of E. coli and S. aureus decreasing to 8.1% and 10.2%, as determined by the spread plate method (Fig. 6). As expected, only sparse bacterial cells with lysed and wrinkled shapes were found on the PIL functionalized membrane surfaces. The synergistic effect of the bacteria-repelling features in the PIL hierarchical architecture and the bactericidal characteristics of the free quaternary ammonium base from the extended QPEI polymer in the aqueous environment enabled the killing of approaching bacterial cells and release of loosely bound bacterial debris by gentle rinsing, leaving behind a much cleaner membrane surface. Consequently, the PES-g-hbSPG-QPEI and PES-ghbSPG-PDDA membrane containing different concentrations of the remaining quaternary ammonium salts further decreased S. aureus attachment to 2.8% and 1.6%, and E. coli adhesion to 1.8% and 0.8%, respectively. These results, when combined, indicate that the PIL-based polymer coatings are highly efficient in suppressing bacterial attachment, proliferation and thus biofilm formation.

#### 3.4 Antifouling behavior in the PRO process

Frequent backwash, chemical treatment and even membrane replacement are often prerequisite steps towards water remediation in modern membrane separation systems prior to the



Fig. 7 Normalized water fluxes of the PES-TFC and PES-g-hbSPG-QPEI membranes as a function of normalized accumulative permeate volume in the PRO process (blank marker: PES-TFC; solid marker: PES-g-hbSPG-QPEI). The hydraulic pressure difference between the feed and draw solution was 15.0  $\pm$  0.2 bar. No concentration adjustments were made to either the feed or draw solutions throughout the entire test.



Fig. 8 FESEM images of the outer surfaces of the PES-TFC and PES-*g*-hbSPG-QPEI hollow fiber membranes. "Pristine membrane" indicates the fresh membrane as prepared and "cleaned membrane" indicates the fouled membrane after the  $3^{rd}$  backwash cleaning. Backwash cleaning was carried out using DI water under 15.0  $\pm$  0.2 bar for 30 min.

unintended impurities reaching and accumulating on the membrane module.55 To investigate the comprehensive antifouling performance of the pristine and PIL modified membranes, WWRe taken from a local municipal water treatment plant was employed as the feed solution during PRO tests under 15 bar. Fig. 7 shows the plots of the normalized water fluxes of PES-TFC and PES-g-hbSPG-QPEI membranes as a function of the normalized cumulative volume of the permeate. When WWRe is dosed to the feed side of PES-TFC membranes, the water flux of PES-TFC first drops to 90% of the initial value and finally decreases to about 60% of the initial water flux when the normalized accumulative permeate volume reaches 100 L m<sup>-2</sup> in run 1. This phenomenon can be explained by the fast and severe gathering of the contaminants inside the porous structure of the original PES-TFC membrane. In contrast, the PES-g-hbSPG-QPEI membrane exhibits a relatively slower initial water flux decline. Over the subsequent testing period, the water flux slowly decreases and stabilizes at 80% of the initial water flux. The smaller drop in water flux validates that the dual-layer chelating polymer modifications enable the PRO membrane to have a minimum fouling tendency due to the generation of a hydration layer caused by the polyelectrolyte brushes and combined adsorption/exclusion mechanisms.

After each 10 h operation, backwashing by feeding DI water into both sides of the membranes at a  $\Delta p$  of 15 bar at the lumen side for 1 h was carried out. For the subsequent runs, the PES-TFC membrane still retains a higher attraction to various contaminants. In comparison, the PES-g-hbSPG-QPEI membranes become more sluggish and exhibit a limited decline in terms of water flux over the whole testing period. It is worth noting that the final water flux after each subsequent run was lower compared with that of the previous run, which may be attributed to the incomplete removal of foulants during the simple backwashing for both membranes. Eventually, after run 3, the water flux of the PES-TFC drops to 35% of the initial water flux while the water flux of the PES-*g*-hbSPG-QPEI remains at 60% of the initial value, indicating the lower fouling tendency of the dual-layer modified PRO membrane.

Fig. 8 shows the FESEM observations of the exterior surfaces of PES-TFC and PES-*g*-hbSPG-QPEI before PRO fouling tests and after the 3<sup>rd</sup> backwash. The pristine PES-TFC exterior surface is fully porous, which makes it vulnerable to the accumulation of foulants. Even after the 3<sup>rd</sup> backwash cleaning, the exterior surface of PES-TFC is still fully sheltered with a thick coverage of salt crystals, nodules and particles, which can be explained by the sticky bonding of these inorganic foulants to the porous and hydrophobic PES-TFC membrane surface. On the other hand,



Fig. 9 Normalized water fluxes of the PES-TFC, PES-*g*-hbSPG and PES-*g*-hbSPG-QPEI membranes as a function of normalized accumulative permeate volume in the PRO process (blank marker: PES-TFC; triangle maker: PES-*g*-hbSPG; solid marker: PES-*g*-hbSPG-QPEI). The hydraulic pressure difference between the feed and draw solution was 15.0  $\pm$  0.2 bar. No concentration adjustments were made to either the feed or draw solutions throughout the entire test.



Scheme 2 Proposed mechanism of the self-healing property of the poly(ionic liquid) hierarchical structure.

the PIL modified membrane could regain its original morphology after backwash cleaning and only sparse crystals and particles could be observed on the exterior surface of the PES-g-hbSPG-QPEI membrane. Clearly, the PIL functionalized membrane surfaces prove effective in inhibiting foulant adhesion and reproduction.

One intriguing advantage of PIL coating layers lies in the long-term stability and environmentally friendly behavior in aqueous environments. These robust traits of the PES-g-hbSPG-QPEI membranes encouraged us to evaluate the performance of modified membranes after aging in WWRe for two months. Similar scenarios were observed on the aged membrane samples in Fig. 5 for the anti-protein adsorption assays, Fig. 7 for the antimicrobial adhesion tests and Fig. 9 for the antifouling performance in PRO tests. The higher chain mobility of the PIL network endows the underlying PES-TFC membranes with self-healing properties in aqueous environments, in which the edges of damaged interfaces in close proximity would be readily compensated via reversible ion-pair exchange, leading to repeated healing processes, maintained membrane performance and prolonged membrane lifespan upon usage (Scheme 2).<sup>27-31</sup> Self-healing coating layers are self-propellant systems that can revert to their original state after microdamage with a partial or complete recovery of their structural integrity.

### 4. Conclusions

In the present study, the antifouling and self-healing PIL coating layers have been transformed into the engineered PES-TFC hollow fiber membranes by the sequential conjugation of anionic hbSPG and cationic QPEI on the preliminarily fabricated PDA gutter layer by  $CuSO_4/H_2O_2$  oxidation of DA. The stronger and stable  $CuSO_4/H_2O_2$  oxidant resulted in the continuous deposition of small and uniform PDA nanoparticles on the membrane surface with negligible structural defects, tunable thickness and favorable polymerization kinetics. It also enabled large-scale membrane functionalization with consistent performance and feasibility at low industrial cost. The superior antifouling characteristics of the resultant PES-*g*-hbSPG-QPEI membranes were verified by the excellent antiprotein behavior and improved antibacterial performance on

both the non-aged and WWRe aged samples. In PRO tests, slow flux reductions and high flux recoveries after backflushing and hydraulic pressure impulsion on the non-aged and aged membranes were also found. The higher chain mobility of the PIL network endows the underlying PES-TFC membranes with self-healing properties in aqueous environments, in which the edges of damaged interfaces in close proximity would be readily compensated *via* reversible ion-pair exchange, leading to repeated healing processes, maintained membrane performance and prolonged membrane lifespan upon usage.

## Conflicts of interest

There are no conflicts to declare.

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