Controlling biofouling of reverse osmosis membranes through surface modification via grafting patterned polymer brushes

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ABSTRACT

Thin film composite (TFC) polyamide membranes are extensively used as selective barriers in reverse osmosis processes. The major challenge faced with TFC membranes is significant fouling on the surface, which restricts the overall purification performance. To address the fouling problem, we developed novel fouling-resistant surface coatings via polyelectrolyte [poly(allylamine hydrochloride)/poly(styrene sulfonate)] layer-by-layer self-assembly, functionalized with patterned antimicrobial and antifouling/fouling-release polymer brushes. Two types of different polymer brushes, among antimicrobial poly(quaternary ammonium), antifouling poly(sulfobetaine) and fouling-release poly(dimethylsiloxane) (PDMS), were selected and grafted in a checkerboard pattern, with a square feature of 2 µm. The successful patterning and incorporation of different polymer brushes on the membrane was confirmed through X-ray photoelectron spectroscopy analysis. Grafting with sulfobetaine and PDMS significantly increased the hydrophilicity and lowered the surface energy of the membrane, respectively. The fouling-resistant property of the modified membrane was evaluated via static protein (bovine serum albumin) deposition and bacterial (Escherichia coli) cell adhesion tests. Surface modifications proved to diminish protein adhesion and exhibited 70–93% reduction in bacterial cell attachment. This observation suggests that the modified membranes have strong antifouling properties that inhibit the irreversible adhesion of organic and bio-foulants on the membrane surface.

Key words | biofouling, grafting, polymer brushes, reverse osmosis membrane, surface modification

INTRODUCTION

The reverse osmosis (RO) process, which uses semi-permeable membranes to achieve selective mass transport, has become the most versatile and efficient technique to produce fresh water from saline water and other wastewater sources (Fritzmann et al. 2007). As the core of the RO process, the RO membrane exhibits superior performance in removing impurities from sea water (Lee et al. 2011) and industrial waste water, such as boiler feed (Koo et al. 2011), electronic industry effluent (Ndiaye et al. 2005) and pharmaceutical waste water (Radjovicic et al. 2008). The performance of RO membrane largely relies on membrane material and structure (Geise et al. 2010). The most successful and commercially available RO membrane is thin film composite (TFC) polyamide membrane, widely regarded as the ‘state-of-the-art’ (Tiraferri et al. 2012), due to its superior salt retaining capacity and water permeability (Kang et al. 2012). However, a major challenge facing the widespread application of RO technology is membrane fouling, which mainly stems from ubiquitous biological substance and natural organic matter (NOM) in the treatment environment (Rana et al. 2010). Once bacteria adhere to the membrane surface, the process of their metabolite production and colonies growth will degrade membrane material and form irreversible fouling. This fouling undoubtedly compromises the membrane’s longevity and increases the associated energy consumption (Greenlee et al. 2009).
To improve the fouling resistance of TFC membranes, several routes have been proposed, such as improving the interfacial polymerization process (Hermans et al. 2014), modifying the membrane surface through physical or chemical methods (Bruening et al. 2013) and creating new types of hybrid organic/inorganic RO membranes (Saleh et al. 2012). The recent trend for membrane surface modification includes loading antimicrobial nanoparticles with the goal to impart their biocidal properties to polyamide membranes (Mo et al. 2007; Tiraferri et al. 2011; Ben-Sasson et al. 2014), and developing fouling-resistant polymer brush coatings on the TFC layers (Thérien-Aubin et al. 2011). Among all these modification methods, grafting functionalized polymer with the aid of UV, ozone, or plasmas is considered to be relatively stable since novel coating would not easily be removed after a longer period use (Zhou et al. 2013).

Antifouling polymer brushes are widely studied for developing fouling-resistant coatings for membrane surfaces (Mansouri et al. 2010; Rahaman et al. 2014). Since bacterial cell adhesion and their growth on the membrane surface are the governing proponent of biofouling, the coatings are primarily designed either to kill bacteria by ‘antimicrobial coating’, or prevent the settlement of foulants through ‘antifouling coatings’, or to provide weak foulant/surface adhesion thus allowing foulants to be easily washed off, by employing a ‘fouling-release coating’ (Therien-Aubin et al. 2011). Different polymers have been used to reduce attachment and viability of bacteria on surfaces. Polymer bearing quaternary ammonium functionalities have been shown to kill or inactivate bacteria (Kenawy et al. 2007). Zwitterionic polymer like poly(sulfobetaine) have been shown to create antifouling coatings, due to their unique water affinity a layer of strongly bounded water molecules at the interface offers repulsive force limiting the adhesion of proteins (Jiang et al. 2010). This class of brush has already been shown to have superior advantages for fouling control in ultrafiltration membranes (Sun et al. 2006; Kang et al. 2007b). In addition, polymer brushes with low surface energy can also limit adhesion. They provide the surface with a weak foulant/surface adhesion and, as a result, attached bacterial cells can be easily washed off from the membrane surface (Coneski et al. 2013). As a typical, low surface energy polymer brushes, poly(dimethylsiloxane) (PDMS), and perfluorinated (Liu et al. 2011), are commonly considered as the ‘fouling-release brushes’ (Coneski et al. 2013), but are largely overlooked by the membrane research community.

The adhesion strategies for different types of foulants can vary widely, therefore it is important to combine polymer brushes that contain different functionalities for membrane fouling control (Rahaman et al. 2014). Direct grafting of polymer brushes onto the membrane surface may be efficient, but results in a thin active layer (2 nm) and also may negatively impact the structure of the TFC layer (Chen et al. 2013). LbL self-assembly is one of the most versatile techniques for fabricating multilayer composite films without destroying the structure of the original membrane (Decher 1997; Chen et al. 2013). Therefore, in this paper, a novel fouling-resistant coating for commercial RO membranes is developed. The membrane is first modified with polyelectrolytes [poly(allylamine hydrochloride) (PAH)/poly(styrene sulfonate) (PSS)] LbL films, and then the LbL film is functionalized by grafting patterned functional polymer brushes onto the multilayer coating. The proposed functional units, poly(quaternary ammonium), poly(sulfobetaine), and PDMS serve as antimicrobial/antifouling/fouling-release brushes, respectively. The modified membrane surface is characterized via X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) techniques, and their surface properties are assessed through water contact angle and surface energy measurements. Moreover, the fouling-resistant behavior of the modified membrane is evaluated through protein (bovine serum albumin (BSA)) deposition and bacterial (Escherichia coli K12 MG1655) cell adhesion tests. These novel coatings contain functional units that would serve as promising routes for fouling control of RO membrane.

**MATERIALS AND METHODS**

**Materials and chemicals**

PAH; Mw = 15 kDa, 18 wt. % Poly(4-styrenesulfonic acid) in water (PSS; Mw = 70 kDa), [2-(methacryloyloxy)ethyl] dimethyl-(3-sulfopropyl)ammonium hydroxide, (methacryloyloxy)ethyl trimethylammonium chloride, 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTA), azobisisobutyronitrile (AIBN), 4′-azobis(4-cyanovaleric acid)
(ACVA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), 2-hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone, propiolic acid, allyl glycidyl ether, methoxymethanol, sodium hydride, dibromoxylene, sodium azide were purchased from Sigma-Aldrich (St Louis, MO, USA). Methacryloxypropyl terminated PDMS with a viscosity of 3–8 cSt was purchased from Gelest (Morrisville, PA, USA). The commercial TFC polyamide RO membrane (SWC4+) was purchased from Hydranautics Membrane. Deionized (DI) water was obtained from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA, USA).

**Preparation of polyelectrolyte LbL films**

The commercial RO membranes (SWC4+, Hydranautics) were pretreated with 20% isopropl alcohol solution for 20 min, and rinsed with DI water three times, then stored in DI water at 4°C until use. Pretreated membranes were spray coated (at 20 psi) alternatively with dilute polymer solutions of positively charged PAH and negatively charged poly(4-styrenesulfonic acid) (PSS) (Figure 1(b)). Excess polymer was rinsed off with a generous amount of water to ensure one layer of absorbed polymer was affixed to the substrate. The number of bi-layers varied from 5 to 10. The top layer of the LbL film was composed of a modified polyallylamine where 30% of the amine groups are substituted with a propiolic acid. The propiolic moieties bear a triple bond used for further grafting reaction.

**Coating poly(allyl glycidyl ether) intermediate layer to the LbL films**

To increase the grafting density and thickness of the polymer brush, 2 wt% N3-poly(allyl glycidyl ether) (PAGE) solution with methanol as solvent was spray-coated on LbL films surface as intermediate layer to procure an abundance of grafting sites (Figure 1(c)). Triple bonds on the surface of the LbL film reacted with azide groups on N3-PAGE resulting in a tight bind for this PAGE-functionalized layer. The membranes were then immersed in a solution of CuSO4 (1.5 M) and sodium ascorbate (0.5 M) for 8 h at room temperature, followed with methanol and subsequently water rinse.

**Grafting and patterning of the polymer brushes**

The patterning of polymer brushes onto LbL films was performed through Thiol-ene click reaction (Figure 1(d)). The first solution of thiol-terminated polymer (100 mg/mL) was spray-coated with a radical photoinitiator on the PAGE-functionalized LbL film, and then certain regions of the membrane were exposed for 30s to UV light (3,500 uW/cm²) using a checkerboard patterned photomask.

![Figure 1](https://iwaponline.com/jwrd/article-pdf/5/3/326/377405/jwrd0050326.pdf)
with features of 2, 5, 10 or 25 μm. Grafting occurred only in the exposed areas, and no reaction was observed in the unexposed areas. After washing with DI water (or hexane in the case of the PDMS brushes), a second polymer was spray-coated with the UV initiator, and the entire membrane was exposed to UV light. This led to the grafting of the second polymer on the previously unexposed regions.

Membrane characterization

XPS experiments were carried out on surface science instrument model SSX-100. The average elemental compositions were calculated from analyzing results obtained from three different spots on the membrane surface. In Table 1, ‘Quats/sulfobetaine-sulfobetaine’ means the sulfobetaine domains of a binary patterned membrane first with quaternary ammonium followed by the grafting of sulfobetaine in a second step. The ‘Quats/sulfobetaine – quats’ is the quaternary ammonium domain of the same membrane. Surface wettability was evaluated from contact angle measurements of DI water using the sessile drop method (VCA Video Contact Angle System, AST Products, Billerica, MA, USA). The system was equipped with software to determine the left and right contact angles (VCA Optima XE). Surface energy was calculated from the advancing contact angles of water, ethylene glycol and diiodomethane on the membrane surfaces.

Antifouling activities evaluation

Protein absorption tests were conducted by immersing the membrane for 48 h in a 0.5 g/L solution of FITC-BSA in 0.1 M phosphate buffer at pH 7.4 containing 3.5% of NaCl. The amount of protein bounded to the membrane was evaluated by the signal intensity obtained by fluorescence microscopy (Olympus BX41, Tokyo, Japan).

To compare bacterial cell adhesion, E. coli K12 MG1655 was used to evaluate the antibacterial prosperity of membrane according to the following protocol. Firstly, a single colony of E. coli was added into 50 mL LB solution that contained 50 mg/L of ampicillin. The solution was then incubated overnight while shaking (100 rpm) at 37 °C. Then, 1 mL of overnight bacterial solution was poured into 50 mL fresh LB solution containing 50 mg/L of ampicillin. The bacterial solution was then incubated for another 2.5 h at 37 °C to reach the exponential growth phase. Twenty mL of E. coli solution was poured in a sterilized plastic tube and centrifuged at 15,000 rpm for 2 min in three cycles. At each time after centrifugation, the supernatant was discarded and the remaining bacterial cell pellet was resuspended by adding 8 mL of 0.9% saline solution and subsequent vortexing. Finally, an adequate amount of 0.9% saline solution was added and mixed with the bacterial cell pellet by vortexing to ensure a final cell concentration of $10^7$–$10^8$ CFU/mL. The cell concentration was estimated by measuring the optical density (OD) of the solution by UV-vis spectroscopy. The desired OD at 600 nm is 0.3. Then, 5 mL of prepared bacteria solution was placed in a sterile plastic vial. A membrane coupon with ¾ inch diameter was placed inside the mouth of the plastic vial with the active side of the membrane facing the bacterial solution. The vial was then inverted and incubated for 1 h at 37 °C. After incubation, the membrane was rigorously rinsed with synthetic wastewater for 5 s, and was then observed under a fluorescent microscope. At least 10 images were taken across the membrane surface and the average number of cells on the membrane was then normalized across the observed membrane area.

### RESULTS AND DISCUSSION

#### XPS analysis

XPS analyses of both patterned and unpatterned polymer brush-modified membrane surfaces were conducted

<table>
<thead>
<tr>
<th>Modification</th>
<th>N:S</th>
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<tbody>
<tr>
<td>LbL</td>
<td>60:40</td>
</tr>
<tr>
<td>Quats</td>
<td>63:37</td>
</tr>
<tr>
<td>Sulfobetaine</td>
<td>56:44</td>
</tr>
<tr>
<td>PDMS</td>
<td>59:41</td>
</tr>
<tr>
<td>Quats/sulfobetaine – Quats</td>
<td>64:36</td>
</tr>
<tr>
<td>Quats/sulfobetaine – Sulfobetaine</td>
<td>58:42</td>
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<tr>
<td>PDMS/sulfobetaine – PDMS</td>
<td>62:38</td>
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<tr>
<td>PDMS/sulfobetaine – Sulfobetaine</td>
<td>53:47</td>
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(Table 1) in order to analyze the selectivity of the grafting reaction on the patterned membranes. Compared with pure LbL multi-layers, grafting poly(quinuary ammonium) (Quats) on polyelectrolyte bilayers led to an increase in the ratio of nitrogen to sulfur (N:S) content from 0.60 to 0.63. On the other hand, functionalizing polyelectrolyte bilayers with poly(sulfobetaine) brushes resulted in a rise of sulfur content. Since sulfobetaine and quaternary ammonium contains -SO$_3$- and -NH- units, respectively, the variation in the N:S ratio after the grafting reaction confirmed the successful grafting of the polymer brushes onto the membrane surface. By grafting poly(quaternary ammonium) and poly(sulfobetaine) patterned polymer brushes on LbL multi-films, the nitrogen to sulfur ratios of the poly(quaternary ammonium) domains remained almost identical to that of pure poly(quaternary ammonium) brush-modified membrane. Similarly, a nearly identical N:S ratio was observed on poly(sulfobetaine) domains and pure poly(sulfobetaine) functionalized membrane. The XPS analysis of PDMS/sulfobetaine patterned membrane also exhibited similar observations. This demonstrated that there was no contamination of the second polymer brush in the domains patterned with the first polymer brush.

**Water contact angle and protein adsorption test**

The surface wetting phenomena of the membranes modified by LbL films functionalized with different polymer brushes were investigated by contact angle and surface energy measurements. The corresponding organic fouling propensities of the modified surfaces were evaluated via BSA protein adsorption tests. The water contact angle of LbL film remained equal to the virgin polyamide membrane (Figure 2); however, a distinct reduction in protein deposition was observed on this LbL surface (Figure 3). This resistance to protein adsorption of LbL films may be attributed to the greater charge density caused by PAH/PSS polyelectrolyte bilayers. Poly(sulfobetaine) modified membrane surface exhibited a lower water contact angle (32 ± 4) than that of the original polyamide membrane (66 ± 4), and a sharp decrease in protein adsorption (nearly 60%) on the modified surface further confirmed the superior hydrophilic property imparted by poly(sulfobetaine). As mentioned earlier, the zwitterionic units (sulfonate, -SO$_3$-, and amide, -NH-) of poly(sulfobetaine) resulted in the formation of a protein repulsive hydration layer on the membrane surface and hence reduced hydrophobic protein adhesion. A membrane grafted with PDMS brushes possessed lower surface energy (30 ± 2 mJ/m$^2$) when compared with that of the virgin polyamide membranes (45 ± 2 mJ/m$^2$), while showing a significant increase in the water contact angle. Owing to the increased hydrophobicity, the PDMS modified membrane surface exhibited the most protein fouling. However, since the PDMS modified membrane offers a low adhesion force between proteins and the membrane surface, it is expected that adsorbed proteins would be washed off with moderate rinsing. These obvious changes of membrane surface property further confirmed
the success of grafting process. Fabricated polymer brushes severed as a functional coating that imparted the membrane surface with various fouling rejected units to reduce contamination through combining mechanisms.

**Bacterial cell adhesion test**

To assess the antifouling property of modified membrane, a series of static (no pressure, no flow) bacterial cell adhesion tests were performed with *E. coli* K12 MG1655. The results showed that except for the PDMS polymer brush, LbL polyelectrolyte films and other functional polymer brush patterned layers contributed to a significant reduction of bacterial cell adhesion (Figure 4). A substantial bacterial cell deposition on PDMS grafted membrane might stem from the low surface energy of modified membrane. Compared with the individual polymer brush-modified surface, membranes that functionalized with patterned polymers exhibited better biofouling-resistant property. Normalized cell adhesion in the range of 7–30% was investigated on the modified patterned membrane surfaces. This observation suggests that the modified membranes have strong antifouling properties that inhibit bacterial adhesion onto the surface, an irreversible process. This also supports our original hypothesis that the use of low surface energy polymer brushes, in particular PDMS patterned with poly(sulfobetaine) brushes, would allow less bacterial cell deposition as well as the near complete ability to remove attached cells with moderate to rigorous rinsing (normalized cell adhesion is less than 10%). The low surface energy polymer brushes, PDMS, offer weak foulant/surface adhesion force and could serve as effective fouling-release brushes, whereas the sulfobetaine polymer brushes act as an antifouling agent due to their superior hydrophilicity. Both protein and bacteria fouling-resistant results suggest a strong potential in using those novel surface coatings for the control of fouling on RO membranes.

**SEM analysis**

The changes in surface morphology and the antifouling behavior of the modified membranes were analyzed using SEM (Figure 5). As expected, the control polyamide membranes exhibited a uniform ridge-and-valley morphology (Figure 5(a)) that is typical for TFC polyamide membranes formed by interfacial polymerization. The overall surface morphologies of the membranes were not significantly affected after coating with polymer brushes on the LbL film (Figure 5(b)). After contact with a bacterial solution and incubation for 1 h, PDMS and poly(sulfobetaine) patterned membrane surfaces showed preferential cell adhesion on the PDMS domains. On the region grafted with PDMS, a considerable cell attachment was observed, while on poly(sulfobetaine) domains, seldom bacteria deposition was found. This may be because of the hydrophobic nature of a PDMS polymer brush that facilitates hydrophobic bonding of the bacterial cells onto the membrane surface. It was also shown in cell adhesion tests that a PDMS polymer brush patterned membrane achieved good fouling-release properties as attached bacterial cells were released after being rinsed rigorously with water. The same membrane sample, with different domains showing different antifouling property, also supports the successful modification of membrane with patterned polymer brushes.

**Implications and challenges**

Water scarcity is a critical global concern; water reuse and desalination are currently considered as the only effective ways for increasing water resources beyond the hydrological cycle (Shannon *et al.* 2008). Owing to its unique separation performance, RO membranes play an irreplaceable role in industry of waste water purification and sea water...
desalination process. However, irreversible fouling caused by NOM and bacteria on membrane surface inhibits their widespread application (Chen et al. 2016). Developing a fouling-resistant membrane will greatly contribute to the overall use of RO techniques and an increase in fresh water supply.

Grafting patterned binary polymer brushes onto the membrane surfaces by using LbL multi-layers as media, as demonstrated in this paper, is an effective strategy for mitigating irreversible fouling. Compared with the direct grafting polymers onto the membrane surface (Kang et al. 2007a; Lin et al. 2010), the physical intermolecular force of LbL films offers stable binding between a membrane surface and polymer brushes without adversely impacting the membrane barrier layer structure, thus maintains the original outstanding separation performance. Although polymer brushes are universally used for membrane antifouling research, their mono-functionalization on a membrane surface exhibit relatively low efficiency. Poly(quaternary ammonium) are the type of biocidal polymers most frequently used; however, their bacterial properties would weaken over time because of a deposited fouling layer produced in the ‘contact killing’ process (Li et al. 2006). Poly(sulfobetaine) is another widely used polymer to reduce cell deposition on membrane surface through its unique zwitterionic property, where a 50% reduction of cell attachment was reported (Chen et al. 2010). In contrast, the combined grafting of antibacterial with fouling-release/antifouling polymer brushes showed excellent antibacterial cell reduction in this paper (71–85% reduction). Combining patterned polymer brushes can reduce the adhesion of protein and cells from various mechanisms and significantly improve the lifespan of functional units. Polymer brushes grafting also presents advantages on modification process, it needs only a few minutes for a reaction, and also the price of polymer is significant lower than biocidal nanoparticles, such as silver, gold or carbon nanotubes.

Nonetheless, the stability of LbL multi-layers is a big challenge of this novel coating, since salt ions in water may impact the interaction of polyelectrolytes. Even though previous studies (Chen et al. 2013) have shown that LbL formed
by 10 bilayers are stable in saline water for 74 days during reverse osmosis process, further experiment is needed to observe the long time performance of functionalized polymer brushes on the membrane surface. An effective modification process is another challenge facing the grafting method. However, the grafting method used in this study is highly scalable and could be implemented in a roll-to-roll process since the required UV irradiation dose is very low.

CONCLUSIONS

The change in nitrogen to sulfur ratio (N:S) observed on different polymer brush-modified areas confirms the successful patterning of polymer brushes on the LbL film. Also, consistent N:S ratios of pure and patterned polymer brush-modified membrane surfaces indicate that there was no contamination of the second polymer brush in the domains patterned with those of the first polymer brush.

Biocidal quaternary ammonium and zwitterionic charged poly(sulfobetaine) brushes significantly lowered the contact angle of membrane surface, and subsequently resulted in the reduction of protein deposition. PDMS modified surface with lower surface energy exhibited an excellent fouling-release property.

In general, surface modifications with different types of polymer brushes resulted in a significant reduction of bacterial cell adhesion. However, PDMS and poly(sulfobetaine) polymer brushes patterned surface showed excellent antifouling properties (normalized cell attachment 7%, compared to 100% for virgin membrane).

Overall, both antifouling and fouling-release results suggest the potential of using this novel surface coating for controlling membrane fouling.

REFERENCES


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