Robust surface stability and enhanced anti-fouling property on PVDF ultrafiltration membrane surface: PDA/PEG co-deposition versus traditional PDA coating

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Abstract. Membrane surface design, especially for the anti-protein fouling property, is vital for the development of synthetic polymer ultrafiltration membranes. Although mussel-inspired antifouling coatings have obtained rapid development, the surface chemical adhesion stability still suffers from weak chemical stability especially in strongly alkaline environment. In this paper, the surfaces of polyvinylidene fluoride (PVDF) membranes were modified via traditional polydopamine (PDA) coating followed with polyethylene glycol (PEG) immobilization method and PDA/PEG co-deposition strategy. In contrast to general PDA coating, the fabricated membrane surface exhibits excellent chemical adhesion stability under the different solution environment (whatever in neutral deionized water solution, acidic solution (pH=2) or strongly alkaline solution (pH=14)). The membrane surface elementary composition and morphologies were evaluated by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The modified membranes obtained via co-deposition were confirmed to have excellent hydrophilicity, enhanced coating stability and good dynamic/static anti-protein adhesion properties. Overall, this work provides a facile, robust and useful bio-inspired anti-fouling membrane surface modification strategy for broadening the application in water treatment field of ultrafiltration membranes.

1. Introduction
The pollution of ultrafiltration membranes has restricted the further application in wastewater treatment field. Membrane materials design modification has become the research hotspot. In contrast of the instability of bulk blending methods and the harsh operating conditions of surface chemistry methods, surfaces modification via mussel-based bioinspired strategy has attracted extensive research interests of experts and scholars due to its environmentally friendly multifunctional coatings[1-4].

Studies has proved that 3,4-dihydroxy-l-phenylalanine (DOPA) has the strong adhesion, and can be easily fabricated polydopamine (PDA) coatings onto the surface of the membranes. Meanwhile, based on the Michael addition and Schiff base reactions, the PDA coatings can mildly react between materials with phenol, amine and thiol group active functional group et al., which provided a strong affinity between PDA layer with organic matter surfaces[5-8]. Among the reported functional molecules, polyethylene glycol (PEG), PEG-based hydrophilic polymers and zwitterionic polymers were the used mostly for fabricating secondary functionalization group onto PDA coatings[9-12]. For
example, Bryan et al. [11] researched the influence of PDA deposition and PEG grafting on pure water flux and bovine serum albumin (BSA) adhesion of the prepared polysulfone ultrafiltration membranes. Daniel and co-workers [12] built active PDA coating by polyethylene glycol monoamine (PEG-NH₂) to obtain desired flux and rejection and finally enhanced significantly fouling-resistant on membrane surface. However, PDA deposition process is time-consuming and unstable in polar organic solvents, especially in strong acidic and alkaline solution media[13-14]. Under this circumstance, secondary functionalization after PDA coated membrane surface will be limited by the modified materials. As a consequence, it is very important to develop a time-rapid and process-facile strategy for PDA coatings with robust surface adhesion stability. Meanwhile, the anti-bacterial structure design is still needed to endow the membrane surface with excellent anti-bacterial performance on the base of anti-protein properties.

In this paper, we report a novel mussel-inspired anti-protein fouling membrane surface design strategy instead of the traditional PDA coating method. In which polyvinylidene fluoride (PVDF) was selected as the ultrafiltration membrane material because of its thermal stability, chemical stability and high mechanical strength properties, and then PVDF membranes were modified via PDA/PEG co-deposition method to fabricate a strongly adhesive anti-protein coating layer. The character of PDA and PEG on membrane surface was evaluated by XPS and SEM. The surface chemical adhesion stability, hydrophlicity, dynamic and static anti-protein adhesion property of all membranes were also studied.

2. Experimental

2.1. Materials
PVDF (TA-1010) was purchased from Solvey Co. Ltd. Dopamine hydrochloride and PEG (99.9%) were received from Sigma-Aldrich. BSA was obtained from Heowns biological Co. Ltd. All other chemicals were provided by commercial sources for analytical specification and were used as received.

2.2. Fabrication of modified PVDF membrane
Home-made PVDF membranes (named as PVDF), PDA modified PVDF membrane (named as PVDF/PDA) and PDA modified PVDF membrane with followed PEG grafting membranes (named as PVDF/PDA-g-PEG) were prepared by our previous studies[15-16]. Then the as-prepared M-PVDF membranes were incubated in DOPA and PEG mixed solutions (V:V=1:1, Tris-buffer, pH=8.5) at room temperature for 3h, and after that the obtained membranes were cleaned with deionized water (DW), blowed to dry with nitrogen and stored before using. The fabricated membrane was named as PVDF-PDA/PEG.

2.3. Characterization for the membranes
2.3.1. XPS measurements. XPS were employed to characterize the chemical composition of the membrane surface. Before test, the samples were rinsed with deionized water and were blowed to dry with nitrogen. Then the measurements used Al-Kα as radiation resource (1486.6 eV, take-off angle 45°, ) from test device (PHI5000, ULVAC-PHI Inc., Japan) and binding energies were calibrated using the containment carbon (C1s = 284.6 eV).

2.3.2. FE-SEM measurements. SEM measurement (Hitachi S-4800, Japan) was employed to observe the surface and cross-sectional morphologies of the modified PVDF membrane. The samples selected were cut into pieces of 0.5×0.5cm², then pasted onto specimen stage, and finally sprayed with gold treatment before test.

2.3.3. Water contact angle and surface adhesion stability measurements. Water contact angle (WCA) measurement was tested on a static water contact angle device (Krüss GmbH, Germany). 2.0 μL of
deionized water droplets was placed onto the membrane surface using a syringe at room temperature and following all results were recorded by a high-speed video measurement. Membrane surface chemistry adhesion stability was evaluated by WCAs change from PVDF, PVDF/PDA, PVDF/PDA-g-PEG and PVDF-PDA/PEG membranes after immersing in neutral deionized water solution, acidic solution (pH=2) and strongly alkaline solution (pH=14) with agitation 200 rpm.

2.3.4. Protein adhesion measurements. The protein adsorption experiments were tested through BSA. Static BSA adsorption and dynamic BSA cycle filtration of the membranes measurements were used to evaluate the anti-protein fouling property, in which the experiment procedures and methods were described in detail from our previous works[15-16].

3. Results and Discussion

3.1. Chemical compositions of the membrane surfaces

Figure 1 showed the wide-scan XPS spectra and surface elemental compositions of the membranes. It was shown that peaks of carbon (C), oxygen (O) and fluorine (F) appeared at all the membranes. In contrast of PVDF membrane, a new peak at 400 eV for nitrogen (N) appeared in the spectra of the modified membranes, which was contributed to PDA coating on membrane surface. As can be seen at the top right of the figure, the amount of N element on PVDF/PDA, PVDF/PDA-g-PEG and PVDF-PDA/PEG membranes were about 4.60%, 3.82% and 4.69%, respectively. And the amount of N element on PVDF-PDA/PEG membrane was more than that on PVDF/PDA-g-PEG membrane, which demonstrated that the PDA and PEG co-deposition was more stable on membrane surface via chemical cross-link reaction. Therefore, these results confirmed that PDA and PEG were successfully fabricated onto PVDF membrane surfaces.

Table 1. Surface elemental compositions of the membranes

| Membrane ID    | C   | O   | F   | N   |
|----------------|-----|-----|-----|-----|
| PVDF           | 42.33 | 4.61 | 53.06 | —   |
| PVDF/PDA       | 46.39 | 6.02 | 42.99 | 4.60|
| PVDF/PDA-g-PEG | 45.40 | 7.84 | 42.94 | 3.82|
| PVDF-PDA/PEG   | 45.87 | 9.27 | 40.17 | 4.69|

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3.2. Morphological characterization of the membranes

Figure 2 showed the surface and cross-sectional morphologies of the membranes. As can be shown, the cross section of PVDF membrane exhibited a asymmetric structure, which contained thin skin layer, few finger-like pores and many sponge-like pores. And this structure provided the membrane matrix with high resistance to pressure and tension. As for the surface images, M-PVDF membrane contained micropores which was contributed to the PVP pore-forming effect during the membrane
formation from coagulation bath. We can also see from the figure that the pore size and porosity of modified membranes had a slight reduction after modification, which will be beneficial for maintaining a good permeability.

![Figure 2. Surface and cross-sectional SEM morphologies of the membranes](image)

3.3. Hydrophilicity and Surface adhesion stability

![Figure 3. WCA images of the membranes rinsed by solutions with different pH values for 12h (1: PVDF; 2: PVDF/PDA; 3: PVDF/PDA-g-PEG; 4: PVDF-PDA/PEG).](image)

Figure 3 showed that the initial WCA values of the membranes (PVDF: 90±1.5°; PVDF/PDA: 68±1.1°; PVDF/PDA-g-PEG: 55±0.6°; PVDF-PDA/PEG: 46±0.4°). The high WCA value of PVDF membrane was due to its inherently hydrophobic feature. The WCA of PVDF/PDA membrane was significantly reduced to ~68° after PDA coating, which was because that the hydrophilic quinone-based groups on membrane surface provided the hydrophilicity. And the WCA values had a furtherly decrease for both PVDF/PDA-g-PEG and PVDF-PDA/PEG membranes owing to the introduction of PEG onto membrane surface. Moreover, We can also see from figure 3 that the WCAs of PVDF, PVDF/PDA, PVDF/PDA-g-PEG and PVDF-PDA/PEG membranes under acidic solution (pH=2) were about 84°, 64°, 51° and 43°, respectively. The results were similar to the WCAs in neutral deionic water environment, which indicated that all the membranes exhibited excellent surface adhesion stability in acidic environment. In contrast, the WCAs of the PVDF, PVDF/PDA and PVDF/PDA-g-PEG membranes showed a great increase under alkaline solution (pH=14), while the WCA of PVDF-PDA/PEG membrane was almost no change and showed chemical adhesion stability under different solution environment (whatever in neutral deionic water solution, acidic solution (pH=2) or strongly alkaline solution (pH =14)). In addition, the PVDF-PDA/PEG membrane was also prepared rapidly than traditional PVDF/PDA-g-PEG membrane, and provided a time-saving PDA modified membrane. Therefore, PDA/PEG rapidly co-deposition coatings endowed PVDF membrane with significant surface adhesion stability.
3.4. Anti-protein fouling properties

Table 2. Static BSA adsorption and dynamic BSA cycle filtration of the membranes

| Samples            | FRR(%) | Third cycle |
|--------------------|--------|-------------|
|                    |        | Ri          | Rf          | Rir         |
| PVDF               | 64.05  | 0.42        | 0.04        | 0.38        |
| PVDF/PDA           | 81.41  | 0.27        | 0.10        | 0.17        |
| PVDF/PDA-g-PEG     | 87.72  | 0.25        | 0.15        | 0.10        |
| PVDF-PDA/PEG       | 91.67  | 0.23        | 0.17        | 0.06        |

Table 2 showed the static BSA adsorption and dynamic BSA cycle filtration of the membranes. As we can see, BSA static adsorption amount of the modified membranes (PVDF/PDA: ~50μg/cm²; PVDF/PDA-g-PEG: ~37μg/cm²; PVDF-PDA/PEG: ~30μg/cm²) was significantly decreased than that of the PVDF membrane (~120μg/cm²), which was attributed to the hydration layer formation between water and the hydrophilic groups such as catechol, carboxyl and quinone groups etc. on modified membrane surface. And the PVDF-PDA/PEG membrane also presented reduced BSA static adsorption amount than that of PVDF/PDA-g-PEG membrane because of the stronger surface adhesion stability and enhanced hydrophilicity. Moreover, the dynamic BSA cycle filtration measurement results were also shown in table 2. The results indicated that, the modified membranes showed high flux recovery ratio (FRR) (PVDF/PDA: ~82%; PVDF/PDA-g-PEG: ~88%; PVDF-PDA/PEG: ~92%) during the third cycle and lower fouling index percentage (PVDF/PDA: 0.27; PVDF/PDA-g-PEG: 0.25; PVDF-PDA/PEG: 0.23) than that of PVDF membrane (FRR: 64%; R: 0.42), which also indicated that part of irreversible fouling from modified membranes has converted into reversible fouling compared with PVDF membrane. The reason was that the membrane surfaces were more hydrophilic to restrict protein attached onto membrane surface and uneasy to be blocked membrane pores during cycle filtration than that of the PVDF membrane, thus endowed membrane surfaces with excellent anti-protein fouling property.

4. Conclusions

In this study, we successfully fabricated anti-protein fouling PVDF ultrafiltration membrane with excellent chemical adhesion stability via PDA/PEG co-deposition. The result has confirmed that the modification was fabricated successfully and the process was greatly time-saving. And the fabricated membrane surfaces exhibit excellent chemical adhesion stability under the different solution environment (whatever in neutral deionic water solution, acidic solution (pH=2) or strongly alkaline solution (pH=14)) due to the covalently cross-linking. The results also showed that the novel PVDF membranes had good hydrophilicity, enhanced resistance to protein attachment, and good dynamic/static anti-protein adhesion properties. All in all, this paper may provide a novel bioinspired co-deposition strategy to fabricate a facile, robust and useful ultrafiltration membrane and broaden the application of ultrafiltration membranes in water treatment field.

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