



Facile sol-gel coating process for anti-biofouling modification of poly (vinylidene fluoride) microfiltration membrane based on novel zwitterionic organosilica



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ABSTRACT

Present study proposed a novel strategy for membrane anti-biofouling modification based on facile sol-gel coating process and antifouling zwitterions. To this end, a novel zwitterionic organosilica monomer (zBPGH) was synthesized. Based on this, membrane was modified with zwitterionic organosilica through sol-gel coating process for conferring the surface anti-biofouling property, namely PVDF-c-pzBPGH. Then the surface physical and chemical properties were investigated by attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). The results demonstrated that uniform and smooth organosilica xerogel coating was formed on membrane surface and the zwitterions were successfully introduced onto the membrane surface via coating. The water contact angle and hydration capacity measurements indicated that the zwitterions endowed PVDF-c-pzBPGH surface excellent hydrophilicity. Results of three-cycle filtration test revealed that PVDF-c-pzBPGH exhibited excellent and long-term antifouling ability to protein and polysaccharide with flux recovery rates of 67.76% and 90.66% respectively after three cycles of fouling. Moreover, the bacterial attachment test showed that PVDF-c-pzBPGH also possessed outstanding anti-bioadhesion ability. Such excellent anti-biofouling ability was mainly attributed to its zwitterionic surface; meanwhile the smoothing effect of coating can also play a role. Overall, this study provided a facile approach for improving the anti-biofouling ability of membrane.

1. Introduction

Owing to the advantages of high separation efficiency and effluent quality, no chemical additive and phase change, simple in operation and low energy consumption, membrane techniques have been widely applied in wastewater treatment by itself or in collaboration with other processes (such as membrane bioreactors) [1]. However, membrane fouling is still a challenge restricting the sustainable development of membrane technology. Membrane fouling could cause a series of operation problems, such as decline of permeability and selectivity, increased operating pressure and cleaning frequency, ultimately resulting in shortening of membrane lifespan and increased operation cost. In general, membrane fouling can be classified into inorganic fouling, organic fouling and biofouling [2]. Among them, biofouling was considered as the most serious fouling problem [3,4]. Extracellular

polymeric substances (EPS) adhesion and accompanied microorganisms attachment are the main contributors of biofouling [5,6]. EPS are macromolecular compounds which not only help the microbial adhesion on surfaces [7] but also cause membrane fouling by forming dense cake layer. Besides, attached microorganisms also can grow, multiply and relocate on the membrane surface, leading to more severe fouling [8].

It is generally acknowledged that the surface hydrophilization is a promising strategy to resist biofouling [1,9], because hydrophilic surface can form a hydration protective layer on membrane surface which can minimize the interaction between biofoulants and membrane surface [10,11]. To this end, various hydrophilic modifiers have been directly or indirectly introduced to membrane surface, including organic polymer material (like polyvinyl alcohol [12], polyethylene glycol derivatives [13], zwitterionic polymers [14], etc.) and inorganic

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nanoparticles (such as TiO₂ [15], SiO₂ [16], carbon nanotubes [17], graphene oxide [18], etc.). Among them, zwitterionic polymer was recognized as a promising candidate and attracted lots of attention in recent years [5,19,20].

Zwitterionic polymer, inspired by phospholipid bilayer of cell membrane, usually contains paired anionic and cationic groups with overall charge neutrality [21]. It has been acknowledged as the next-generation of antifouling material because zwitterion can strongly bind water molecules via electrostatic interaction [2], which is much stronger than hydrogen bonds interaction [22], to form dense and steady hydration layer that can effectively inhibit the biofoulants adsorption. Additionally, recent studies demonstrated that zwitterionic polymer containing cationic quaternary ammonium (N⁺) also possessed bacteriostatic property which especially benefit the anti-biofouling performance [5,23]. A variety of strategies have been successfully employed to introduce zwitterions onto membrane surface, mainly including surface grafting (like transfer radical polymerization (ATRP) [24], photo-initiated [25], ozone-initiated [26], and plasma-initiated radical graft polymerization [27], etc) and surface coating (such as chemical vapor deposition (iCVD) [3], self-assembling [20] and biomimetic adhesion [8], etc). However, they all have respective limitations, such as complicated modification processes, plugging membrane pores, instability of coating and dependent on substrate material, etc. Therefore, it is still desirable to develop a more convenient, effective and versatile method to introduce the zwitterions onto membrane surface.

Silica-based sol-gel coating process is a facile and versatile surface modification technique, which requires facile operating conditions and produces coating with high adhesion stability to various materials [28–31]. Generally, the sol could be prepared through a controllable hydrolysis and condensation of siloxane group in liquid phase. The nanoscale size of the sol particle enables it excellent adhesion to substrate surface, furthermore subsequent condensation and curing at interface can produce better bonded and stable xerogel coating on substrate surface [32]. Recently, based on the inherent advantages of silica-based coating, organosilica (referred to organically modified silica) coating was designed to meet different antifouling requirements [33–35]. Organosilica is inorganic-organic composite at molecular level that combines the basic advantages of inorganic silica-based coating and the antifouling properties of organic groups [36]. Generally, organosilica monomer (empirical formula of R'_nSi(OR)_{4-n}) contains a hydrolyzable siloxane group Si(OR)_{4-n} and a reactive substituents R', where siloxane group can form inorganic sol-gel coating by hydrolysis and condensation, and by changing the organic R' moiety the coating can be endowed with antifouling function. Typically, poly(ethylene glycol) (PEG) as representative hydrophilic polymer with antifouling properties was reported to be incorporated with silica-based coating for the purpose of enhancing surface antifouling properties, especially the protein resistance ability [34,37]. Owing to its coating stability and antifouling property, organosilica coatings have been successfully employed for preventing biofouling in marine shipping and biomedical devices [38,39], whereas its application on filtration membrane was rarely reported.

Given these, a novel strategy for anti-biofouling modification of filtration membrane by combing the silica-based sol-gel coating process and zwitterions was proposed in present study. To this purpose, novel zwitterionic organosilica monomer was synthesized by structuring zwitterion group as the organic substituent R' of organosilica. Based on which, zwitterionic organosilica composite was prepared and then coated on the membrane surface through a facile sol-gel coating process for anti-biofouling modification. To our best knowledge, such a modification strategy for membrane surface has never been addressed. In this study, the surface morphology, chemical compositions, hydrophilicity, and pure-water permeability of the modified membranes were assessed and discussed. In addition, the anti-biofouling capacity of the modified membrane was evaluated in terms of its resistance to protein,

polysaccharide and microbial fouling; meanwhile relationship between anti-biofouling properties and membrane surface characters was also investigated.

2. Materials and methods

2.1. Materials

(3-Glycidyloxypropyl) triethoxysilane 1, 6-diaminohexane and 3-bromopropionic acid were purchased from Sigma-Aldrich and used as received. Tetrahydrofuran (THF) used for organosilica monomer synthesis was purchased from Sigma-Aldrich and then distilled from sodium to keep it anhydrous. Phosphate buffer saline (PBS), bovine serum albumin (BSA), and sodium alginate (SA) were purchased from Shanghai Aladdin Reagent Company and used as received. All other chemicals (NaCl, CaCl₂, glutaraldehyde, NaClO, ethanol and hexane) were of analytical reagents grade and were used without further purification. PVDF microporous membranes with average pore size of 0.1 μm was supplied by Motimo membrane technology Co., Ltd. Deionized water (minimum resistivity of 18.0 MΩcm) used throughout the experiment was obtained from a Millipore water purification system.

2.2. Synthesis of zwitterionic organosilica monomer: zBPGH

The synthesis route of zBPGH is described in Fig. S1. First, the random organosilica monomer 1,6-bis(triethoxysilylpropylglycidylamino) hexane (BPGH) was synthesized by the ring opening reaction of (3-Glycidyloxypropyl) triethoxysilane (GPES) with 1,6-diaminohexane. Typically, a solution of 1,6-diaminohexane (2.9 g, 0.025 mol) in anhydrous THF (50 mL) was added into a 250 mL three-necked flask with stirrer and thermometer. Then the solution of GPES (27.8 g, 0.1 mol) in anhydrous THF (50 mL) was added dropwise into the flask at 55 °C over 5 h. Afterwards, the reaction mixture was stirred at 55 °C for another 24 h with nitrogen protection. To obtain pure tetramer-bridged monomer BPGH, slightly overdose of GEPS was adopted. The residual GEPS was removed by the amine modified silica gel [40]. The modified silica (10 g) was added into the solution of the products, stirred at 55 °C for 5 h, the epoxy groups of excess GEPS could react with the amines on the silica gel, and then filtered to get the pure BPGH products. In order to identify the molecular structure of BPGH, ¹H NMR spectra of BPGH was collected using a 400 MHz Bruker Spectrometer and was shown in Fig. S2. ¹H NMR (400 MHz, CDCl₃): δ = 3.81 (dd, 2H, J = 13.7, 6.8 Hz), 3.42 (m, 16H), 2.59 (m, 12H), 1.69 (m, 8H), 1.46 (s, 4H), 1.21 (t, J = 6.8 Hz, 40H), 0.63 (dd, J = 15.4, 7.0 Hz, 8H). BPGH possesses four bridged siloxane groups, which can form high-level cross-linking inorganic silica framework through hydrolysis and condensation, thereby improving the adhesion strength and curing rate of coating. Besides, the two active tertiary amine contained in BPGH can serve as reactive sites for coupling of various functional group, such as structuring zwitterion by a readily quaternisation reaction with 3-bromopropionic acid.

Second, to obtain zwitterionic BPGH (zBPGH), a solution of 3-bromopropionic acid (7.6 g) in anhydrous THF (50 mL) was added into BPGH solution (30.7 g in 50 mL anhydrous THF) and stirred at 50 °C for 24 h with nitrogen protection. Then, the solution was precipitated in excess hexane. The dissolution-precipitation procedure was repeated three times, yielding a yellowish-brown product. Finally, the product was dried under reduced pressure to a constant weight. With the aim to identify the zwitterionization of BPGH, ¹³C NMR spectra of zBPGH product was collected and displayed in Fig. S3. ¹³C NMR (100 MHz, CDCl₃): δ = 169.8, 73.5, 71.8, 69.8, 67.9, 58.3, 58.1, 34.9, 25.5, 22.9, 22.8, 18.2, 6.5, 6.4.

2.3. Preparation of zwitterionic organosilica composite: poly-zBPGH

The poly-zBPGH was prepared by precisely controlled sol process. The properties of the sol, such as viscosity and particle size which

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