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Immobilization of poly(*N*-acryoyl morpholine) via hydrogen-bonded interactions for improved separation and antifouling properties of poly (vinylidene fluoride) membranes

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ABSTRACT

Poly(*N*-acryoyl morpholine) (PACMO), a promising antifouling surface modifier, has many desirable properties including high hydrophilicity, chemical stability, and excellent hemocompatibility. Considering the intrinsic hydrophobic property of most polymer membranes, surface modification by hydrogen bonding self-assembly has garnered intense interest. In this work, a hydrophobic poly(vinylidene fluoride) (PVDF) membrane surface was first dip-coated a polydopamine (PDA) coating and then followed by immobilization of PAMCO via hydrogen-bonded interactions between PACMO and PDA. The mechanism of foulants deposition onto the membrane surface was quantitatively assessed by extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory. The hydrophilic PACMO layer modified PVDF membranes exhibited a simultaneously enhanced permeability, rejection and antifouling property in protein filtration and oil/water emulsion filtration, and humic acid filtration, respectively. Moreover, the as-prepared membranes had prominent long-term stability even in harsh conditions due to strong hydrogen-bonded interactions between PACMO and PDA. This work provided a practical strategy for hydrophilizing membrane surfaces by hydrogen bonding self-assembly.

1. Introduction

Membrane technology has a promising novel route to cope with freshwater scarcity and energy consumption due to its principal superiorities [1,2]. Polymer membranes have a myriad of applications in environmental, biomedical, and energy fields with regard to excellent combination of properties [3,4]. However, membrane fouling is a severe and ubiquitous issue hampering the sustainability of membrane technology because it can lead to tremendously decline of permeability and productivity at a fixed transmembrane pressure, ultimately increase additional hydraulic resistance [5,6]. In general, membrane foulants can be classified into proteins, emulsified oils, microorganisms, and humic substance fraction of natural organic matter due to various attractive forces between the foulants and the membrane [7]. These foulants usually have a conspicuous susceptibility for adhesion to hydrophobic membrane than hydrophilic membrane on the surface or/and in the pores. Hence, it is necessary and meaningful to modify membrane surface for hydrophilizing a hydrophobic membrane surface.

It is well recognized that nonionic polymers, such as poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA), poly(*N*-vinyl pyrrolidone) (PVP), and poly(*N*-acryoyl morpholine) (PACMO) have been broadly introduced into the membranes to elevated hydrophilicity [8–13]. The antifouling behavior of nonionic polymer is interpreted with hydration layer stemmed from hydrogen bonds between nonionic polymer and water molecules, and that electrically neutral is most resistant to organic foulant adhesion due to hydrogen bond acceptor property [14,15]. Two straightforward approaches, bulk modification and surface modification, have been achieved to incorporate nonionic polymers into and/or onto polymer membranes [16]. PEG was used as an additive to fabricate sulfonated poly(phenylene sulfone) (PPSU) membranes via non-solvent induced phase separation [17]. The as-prepared membranes possessed improved mechanical strength, hydrophilicity and permeation properties with an appropriate amount of PEG in the dope solution. Similarity, PVA was blended with poly(ether sulfone) (PES) matrix to improve the fouling resistance during the membrane-forming process [18]. The blended nonionic polymer also incorporated into the dope solution as a pore forming agent, which was eluted out after membrane solidification. To solve this problem, some amphiphilic copolymers containing nonionic polymer ingredient as hydrophilic moiety were investigated. The hydrophilic nonionic polymer chains of

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amphiphilic copolymer could be better immobilized in the membrane matrix, and simultaneously prolonged the hydrophilicity of membranes. For instance, Qin et al. [19] synthesized amphiphilic poly(vinylidene fluoride)-*graft*-poly(*N*-vinyl pyrrolidone) (PVDF-*g*-PVP) copolymer via irradiation induced graft polymerization and used as an additive to produce PVDF membranes. Liu et al. [20] synthesized amphiphilic poly(vinylidene fluoride)-*graft*-poly(*N*-acryoyl morpholine) (PVDF-*g*-PACMO) copolymer via radical polymerization and then directly used to prepare membranes without the blending of PVDF homopolymers. Shen et al. [21] also fabricated PVDF-*g*-PACMO copolymer membranes with *N*-acryoyl morpholine monomers via atom transfer radical polymerization (ATRP). The copolymer membranes exhibited many desirable properties including high hydrophilicity, chemical stability, and good hemocompatibility. However, the aforementioned strategies still suffered from the difficulty to control the grafting uniformity because there were no active functional groups in nonionic polymer [22]. The extra pretreatment and reagents were used to demand for intricate syntheses of the amphiphilic copolymers and were merely effective for small scale development in laboratories. Therefore, it is necessary to explore a more facile, versatile, and larger-scale production method for constructing hydrophilic membranes with nonionic polymers.

Recently, hydrogen-bonded interactions provided a complementary approach to immobilize nonionic polymers for hydrophilic membranes [23–26]. The hydrogen-bonded interactions are noncovalent self-assembly, avoiding complex chemical reactions during preparation processes. Moreover, nonionic polymer can be precisely adjusted by the density of hydrogen bonding originated from the change of ingredient concentration and self-assembly time by varying fabrication conditions. Fan et al. [23] prepared the hydrophilic membranes by m-trihydroxybenzene hydrogen-bonded interactions between PES matrix and PEG, endowing more robust hydrophilicity. Apart from the bulk modification, hydrogen-bonded interactions could also be directly used for surface modification of hydrophobic membranes. Huang et al. [24] anchored PVP on the alkaline-treated PVDF membrane surface via the hydrogen-bonded interactions, which possessed the lactam group of PVP, allowing it to interact with the hydroxyl groups of PVDF. Jiang et al. [25] immobilized a PVP layer on the polydopamine (PDA) coated polypropylene (PP) membrane surface via the hydrogen-bonded interactions between the lactam groups of PVP and the catechol groups of PDA, endowing the membranes with enhanced hydrophilicity, permeation and protein resistance. Wu et al. [26] employed a metal-polyphenol precursor layer to immobilized PVP on the polyamide (PA) reverse osmosis membrane surface by the hydrogen-bonded interactions between the PVP and the precursor layer. The above composite coatings were supposed to self-assembled monolayer, which containing hierarchical structure was the most resistant to the adhesion of foulants. However, PACMO has not been immobilized onto the membrane surfaces via hydrogen-bonded interactions to enhance the fouling resistance. Fortunately, PACMO is a strong hydrogen acceptor, which probably could be anchored onto the hydrophobic membrane surface inspired by the hydrogen-bonded interactions.

Owing to the inherent hydrophilicity, the PDA coating as an intermediate layer has been widely utilized to construct a better hydrophilic surface [27–29]. The abundant catechol groups on the PDA coating probably could contribute to the formation of strong hydrogen-bonded interactions with PACMO, the strength of hydrogen-bonded interactions between amide groups in PACMO and catechol groups in PDA were less influenced by the pH or ionic strength as comparable to covalent interactions [30–32]. The formed coating, as a self-assembled monolayer, is possible to avoid the decrease of membrane permeability when modification is properly completed by varying fabrication conditions. Herein, a hydrophobic PVDF membrane surface is first dip-coated a PDA coatings and then followed by immobilization of PAMCO via hydrogen-bonded interactions between PACMO and PDA. The hydrophilicity of the PVDF/PDA-PACMO membranes can be well tuned by adjusting the content of PACMO. The reasons for the improved hydrophilicity of the membranes are disclosed by a serial of characterizations, and are applied to systematic research surface and interface characteristics of the membranes with low proteins adhesion. The separation performance and antifouling property (BSA protein, oil/water emulsion, and humic acid, respectively) of obtained PVDF membranes have been evaluated. Furthermore, the stability is examined by a long-term water immersing and even in harsh conditions. Considering a more universal surface modification platform, this work will set a success example of the hydrogen bonding self-assembly method for modifying membrane surfaces to improve antifouling and separation performance.

2. Experimental

2.1. Materials and reagents

N-acryoyl morpholine (ACMO) was purchased from MAYA Reagent Co., Ltd., Zhejiang, China. Details of the PACMO homopolymers preparation procedure were provided in Text S1 of the Supporting Information. Dopamine hydrochloride was obtained from Ouhe Technology Development Co. Ltd., Beijing, China. Potassium peroxodisulfate (KPS), lithium chloride (LiCl), and humic acid (HA) were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Tris(hydroxymethyl) aminomethane (TRIS) was purchased from Sigma-Aldrich, pH value of prepared TRIS buffer is 8.5. PVDF powders (Solef 1010, $M_w = 3.52 \times 10^2$ kg mol^{-1}, $M_w/M_n = 2.3$) were obtained from Solvey Company of Belgium. *N*, *N*-dimethylformamide (DMF, Guangfu Technology Development Co. Ltd., Tianjin, China) was used as the solvent. Bovine serum albumin (BSA) having a molecular weight of 68,000 was purchased from Solarbio Science & Technology Co. Ltd., Beijing, China. Rice oil (Golden Dragon Fish) was purchased from a local supermarket. Other reagents were all analytical grade and used without further purification.

2.2. Interactions between PDA and PACMO

Pieces of silicon wafer were cleaned by sonication in ethanol for 30 min followed in deionized (DI) water. The cleaned silicon wafers were then instantly coated with DA (1.0 mg mL^{-1} in TRIS buffer), PACMO (5.0 mg mL^{-1} in TRIS buffer) or DA/PACMO mixture (1/5 wt % DA/PACMO, DA concentration of 1.0 mg mL^{-1} in TRIS buffer) for 1 h with exchange of the solution after 30 min. The samples were continuously shaken during the coating process. The coated silicon wafers were rinsed with DI water, dried under a stream of nitrogen and stored under vacuum for further analysis.

The high-resolution X-ray photoelectron spectroscopy (XPS) measurements were employed to study the surface composition of these samples. XPS was conducted on K-alpha spectrometer (Thermo Fisher, UK) using a monochromatic Al Kα X-ray source (1486.6 eV photons). Three areas of two independent samples were investigated to test the homogeneity of the coatings.

It confirmed the interactions between PDA and PACMO by a UV–vis spectrometer (TU-1810PC, Beijing Purkinje General Instrument Co., Ltd., China). The PDA deposition was collected by centrifugation (8000 rpm) of a 1.0 mg mL^{-1} TRIS buffer of DA after polymerizing at room temperature for 48 h. The product PDA was dried to constant weight in a vacuum oven at 60 °C. Then a 1.0 mg mL^{-1} PDA deposition was added into PACMO solutions of different concentrations (0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mg mL^{-1}) and the mixture was shaken for 24 h. UV–vis absorption bands of the mixture solution were detected from 225 to 700 nm.

2.3. Coating of PVDF membranes using PACMO

In a typical approach, the PVDF flat membrane (labeled as $M_{Pristine}$)