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Nanofiltration membranes via co-deposition of polydopamine/polyethylenimine followed by cross-linking

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ABSTRACT

Novel composite nanofiltration membranes (NFMs) were simply fabricated via co-deposition of mussel-inspired polydopamine (PDA) and polyetheylenimine (PEI) followed by glutaraldehyde (GA) crosslinking. A uniform, robust and defect-free selective layer was generated on the hydrolyzed polyacrylonitrile (HPAN) ultrafiltration membrane substrate, endowing the composite NFMs with high separation performance for multivalent ions. Zeta potential measurements indicate these NFMs are slightly positively charged, resulting in a salts rejection sequence of $MgCl_2 > CaCl_2 > MgSO_4 > Na_2SO_4 > NaCl$ at pH 5.5. The nanofiltration performance can be tuned by changing the co-deposition time and the mass ratio of dopamine/PEI. A mass ratio of 2/2 with 4 h co-deposition is the optimum protocol for the membrane performances including surface hydrophilicity, water flux and salt rejection. Moreover, the composite NFMs show a good structural stability for immersing in ethanol or for long-term nanofiltration process.

1. Introduction

Nowadays, nanofiltration has become a rapidly developing and expanding area with tremendous potential for desalination, water softening and wastewater recycling [1]. In general, nanofiltration is defined as a pressure-driven process with properties between reverse osmosis and ultrafiltration [2]. Due to its special separation properties, nanofiltration owns the advantages of both aforementioned processes including low operation pressure, high flux, high retention of multivalent ions and organic molecular (200–1000 Da) along with low investment, operation and maintenance costs [1,3]. Nanofiltration membranes (NFMs) are mainly fabricated via interfacial polymerization technique [4–8]. It is a facile and fast method to prepare composite NFMs. The resulted active layer can be attached onto various substrates. Nevertheless, the compatibility between the support layer and the skin layer is usually so poor that the skin layer can be easily detached from the substrate in harsh environments containing organic solvents such as ethanol. Great effort has been made to enhance the adhesive strength between the skin layer and the substrate surface, including creating covalent linkage and constructing adhesive transition layer [9–12]. For example, grafting method can strongly binding the active layer onto the substrate by covalent bonds and significantly improve the adhesive strength [13,14]. However, these methods are complicated or far from precisely control. As a consequence, a facile fabrication method is in great demand for composite NFMs with excellent structural stability.

Inspired by the universal adhesion of the adhesive proteins in mytilus edulis foot, Messersmith and his co-workers demonstrated that dopamine could be oxidized in alkaline environment and formed a polymer-like coating on various substrates with great adhesive strength [15–20]. After that, numerous of studies have applied mussel-inspired coating technique into membrane science such as surface modification, functionalization and fabrication of thin film composite membranes [21–30]. Zhu et al. fabricated a novel hydrophilic NFM by simply immersing polysulfone ultrafiltration substrate in dopamine solution [31]. The work of Li et al. further chemically modified the membrane with a fluorinated polyamine after dopamine deposition to obtain a stable composite membrane with good antifouling performance [32]. However, the pure polydopamine (PDA) coating is not dense enough for excellent salts rejection. Scientists then grafted polyethyleneimine (PEI) onto PDA deposited PES membrane with or without further crosslinking to obtain a much denser and more compact composite membrane with good salts rejection performance [33,34]. Nevertheless, it is well known that the deposition process of pure dopamine is generally time-consuming and heterogeneous, the resultant PDA particles are not compactly or uniformly coated on

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the substrate surfaces. These problems have greatly limited the advanced application of PDA coating on the preparation of NFMs.

In our previous study, we found that the addition of low-molecular-weight PEI can reduce the self-aggregation of PDA to form particles and then promote the homogeneous polymerization and deposition of dopamine [29]. In this work, we simply fabricated a novel kind of NFMs with positively charged smooth surfaces via the co-deposition of PDA/PEI followed with cross-linking by glutaraldehyde (GA). We detailedly investigated the chemical structures, hydrophilicity and charge properties, as well as the morphologies of the composite NFMs. These NFMs possess a smooth and dense selective layer, which exhibit high rejection performance (> 90%) for multivalent cations. Furthermore, the membranes even show excellent structure stability for ethanol and long-term operation.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN) ultrafiltration membranes (pore size ranging 40–80 nm, MWCO = 10–30 kDa) were purchased from Shanghai MegaVision Membrane Engineering & Technology Co. Ltd (China). Dopamine hydrochloride and polyethyleneimine (PEI, Mw = 600 Da) were obtained from Sigma-Aldrich (USA) and Aladdin (China), respectively. Other chemicals, including tris (hydroxymethyl) aminomethane, ethanol, sodium hydroxide, hydrochloric acid solution (18 mol/L), glutaraldehyde (GA) solution (50 wt%), inorganic salts, bovine serum albumin (BSA, pI 4.8, 67 kDa) and lysozyme (Lys, pI 10.8, 14.4 kDa) were procured from Sinopharm Chemical Reagent Co., Ltd. All of the chemical agents were used without further purification.

2.2. Membrane fabrication

Fig. 1 presents the fabrication process of the composite NFMs. PAN ultrafiltration membranes were hydrolyzed at first in sodium hydroxide solution (1.5 mol/L) for 60 min at 50 °C, and then immersed into hydrochloric acid solution (2 mol/L) for 1 h at room temperature (25 °C) for acidizing. The hydrolyzed PAN (HPAN) membranes were rinsed by deionized (DI) water for 24 h and then used as support for the composite NFMs. Dopamine hydrochloride and PEI were dissolved in Tris–HCl buffer solution (pH = 8.5, 50) with designed mass ratio. The circular pieces of HPAN membranes with diameter of 4 cm were prewetted by ethanol for 30 min, and then transferred into the fresh prepared dopamine/PEI solution and shaken at 25 °C for certain time. The as-prepared membranes (PDA/PEI-modified membranes) were washed by DI water for several times and dried at room temperature. The cross-linker, GA, was dissolved in ethanol with a concentration of 2 wt%. Afterwards, the PDA/PEI-modified membranes were immersed into it for 20 min at 50 °C followed by post-treatment in vacuum at 50 °C for another 20 min. Finally, the obtained NFMs were rinsed several times and stored in DI water for further characterization and evaluation.

2.3. Membrane characterization

The chemical structures of membrane surfaces were investigated by Fourier transform infrared spectrometer (FTIR/ATR Nicolet 6700). The spectra were collected from 400 to 4000 cm^{-1} by cumulating 32 scans at a resolution of 4 cm^{-1}. More details in chemical components were analyzed by X-ray photoelectron spectrometer (XPS, PerkinElmer, USA) using Al Kα excitation radiation (1486.6 eV). The whole spectra were collected ranging from 0 to 1000 eV with a survey depth of 5–10 nm. The field emission scanning electron microscopy (FESEM, Hitachi, S4800, Japan) was utilized to observe the surface and cross sectional morphologies of the membranes. The membranes were dried and fractured in liquid nitrogen to prepare sectional samples. Atom force microscopy (AFM, MultiMode, Vecco, USA) was employed to probe the roughness of the membrane surface in the tapping mode. The static and dynamic water contact angles were measured by a DropMeter A-200 contact angle system (MAIST VisionInspection & Measurement Co. Ltd., China) at room temperature. A streaming potential method was utilized to detect the charging property of the membrane surface using the electrokinetic analyzer (SurPASS Anton Paar, GmbH, Austria) with KCl (1 mmol/L) solution as electrolyte solution. The pH dependence of surface zeta potential was investigated via adjusting pH by NaOH and HCl

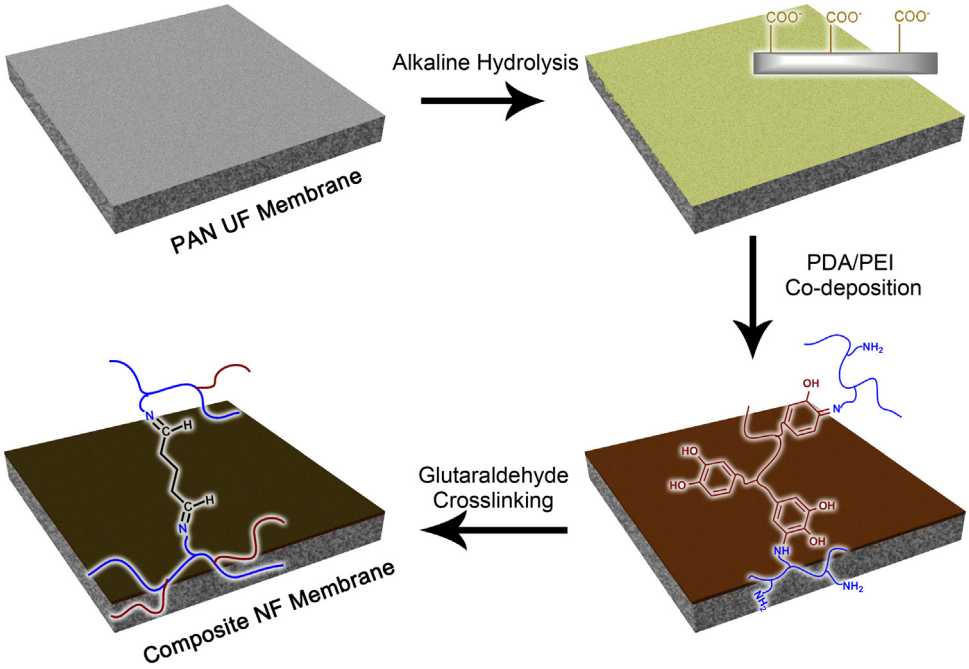

Fig. 1. Schematic diagram of the preparation process and mechanism for the composite NFMs.