



ELSEVIER

Contents lists available at ScienceDirect

## Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

# Preparation of thin film composite nanofiltration membrane with improved structural stability through the mediation of polydopamine

Yafei Li<sup>a</sup>, Yanlei Su<sup>a,b</sup>, Jianyu Li<sup>a</sup>, Xueting Zhao<sup>a</sup>, Runnan Zhang<sup>a</sup>, Xiaochen Fan<sup>a</sup>, Junao Zhu<sup>a</sup>, Yanyan Ma<sup>a</sup>, Yuan Liu<sup>a</sup>, Zhongyi Jiang<sup>a,b,\*</sup>

<sup>a</sup> Key Laboratory for Green Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

## ARTICLE INFO

## Article history:

Received 21 August 2014

Received in revised form

25 October 2014

Accepted 8 November 2014

Available online 20 November 2014

## Keywords:

Polydopamine

Bioadhesion

Structural stability

TFC membrane

Nanofiltration

## ABSTRACT

Thin film composite (TFC) nanofiltration membranes with good structural stability were prepared by interfacial polymerization under the mediation of polydopamine (PD). Polyethersulfone (PES) support layer was firstly modified by PD prior to the interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMC) to form polyamide active layer. PD played the following two important roles: (1) rendering the PES support layer with the reactive groups to enhance the interfacial strength between the support layer and active layer; (2) rendering the PES support layer with higher hydrophilicity to facilitate interfacial polymerization. The TFC membrane prepared under optimal conditions exhibited a flux of 22.8 L/(m<sup>2</sup> h) while the rejection of Na<sub>2</sub>SO<sub>4</sub> reached 93.5% under 0.2 MPa. Particularly, the TFC membrane exhibited good structural stability (less than 5% decline in salt rejection) as tested by alcohol treatment due to the strong interactions between the active layer and the modified PES support layer.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Thin film composite (TFC) nanofiltration membrane, comprising a thin active layer on a porous support layer, has been widely applied in wastewater reclamation, industrial water production and water softening [1–6]. Interfacial polymerization is still the dominant method to prepare TFC nanofiltration membrane, which takes place at water/organic solution interface and forms a thin active layer on the surface of porous support layer [7]. A key advantage of the TFC approach is that the support layer and the active layer can be separately optimized to achieve the best overall separation performance [8]. Despite this, TFC nanofiltration membrane faces one critical technical limitation: the poor interfacial adhesion strength between the support layer and the active layer [9]. Firstly, majority of the active layers are made of hydrophilic materials such as polyamide, polyester, polyurea or polyurethane [10–13], whereas majority of the support layers are made of hydrophobic materials [14–16]. Secondly, the active layer formed by interfacial polymerization is physically adhered on the support layer [14]. Big difference in swelling degree and the weak interactions between these two layers would cause the peeling of active layer from support layer during

long-time operation especially under swollen conditions (in the presence of organic solvents), leading to serious performance damage and a sharp decrease in lifetime of TFC membranes [17]. Hence, it is essential to build a robust interface between active layer and support layer of TFC nanofiltration membrane.

Prior studies relevant to enhancing the interfacial adhesion of TFC nanofiltration membrane can be divided into two categories: (1) increasing the hydrophilicity of support layer for stronger physical interaction with the active layer [14,15,18]. For example, Kim et al. [14] modified PSf and PP support layer by plasma treatment with hydrophilic materials, and prepared polyamide TFC membrane with improved adhesion property via interfacial polymerization; (2) modifying the support layer with functional groups to form covalent/ionic bond with the active layer [19,20]. For example, Oh et al. [21] treated polyacrylonitrile (PAN) support layer with NaOH solution for 3 h to convert –CN to –COOH prior to interfacial polymerization. Modified composite membranes were stable due to the chemical interactions between the –COOH groups and the polyamide layer formed on top of the support layer [19]. However, these methods often involve the complicated pre-treatment steps or harsh pre-treatment conditions, which limit their wide application. A more convenient, efficient method is still required to be explored in order to enhance the interfacial adhesion between active layer and support layer.

Inspired by adhesive proteins of mussels, polydopamine (PD) has drawn much attention as a versatile adhesive platform [22–25].

\* Corresponding author at: Key Laboratory for Green Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. Tel.: +86 22 27406646; fax: +86 22 23500086.

E-mail address: [zhyjiang@tju.edu.cn](mailto:zhyjiang@tju.edu.cn) (Z. Jiang).

Simple immersion of substrates in aqueous solution of dopamine, buffered to alkaline pH, could result in spontaneous deposition of PD [26–28]. The adhesive PD could stick to almost any material surfaces [23] due to the strong and multiple interactions between PD and the substrates, which include covalent and noncovalent interactions such as the hydrogen bonding interaction,  $\pi$ - $\pi$  interaction, and electrostatic interaction [29]. The formation of PD can be easily manipulated by varying dopamine concentration, deposition time or pH of buffer solution [30]. Besides the universal adhesion of PD, another attractive advantage is that the quinone groups in PD could react with thiol-bearing compounds and nitrogen derivatives, enabling the chemical functionalization of any type of material surface [22,24,31]. Recently, PD has been used to increase hydrophilicity of microfiltration, ultrafiltration, nanofiltration and reverse osmosis membranes [24,32–34] or used as a primer layer for further functionalization to improve their antifouling performance [35–37]. PD has also been deposited on hydrophobic membranes prior to coated with cross-linked chitosan for the synthesis of chitosan/polyethersulfone composite pervaporation membrane [38] and coated with cross-linked polyethyleneimine for the synthesis of polyethyleneimine/polysulphone composite nanofiltration membrane [39]. Both separation performance and structural stability of those membranes were increased. PD was also used to modify support layer of TFC membranes to enhance hydrophilicity and reduce internal concentration polarization for use in forward and pressure retarded osmosis [40–42]. Other applications involve using PD as selective layer for nanofiltration, pervaporation, and dehumidification membranes [43–45]. However, no report has been found about modifying support layer with PD “before” carrying out interfacial polymerization to prepare structurally stable TFC nanofiltration membrane and valuing the effect of PD on the structural stability of those composite membrane.

In this study, an approach for preparing structurally stable TFC nanofiltration membrane was explored, which involved simple deposition of PD onto a PES ultrafiltration membrane to form the modified support layer, followed by interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMC) to form polyamide active layer on the modified support layer. PD played the following two important roles: on one hand, the quinone groups on the modified support layer would react with PIP, forming the covalent linkage between active layer and support layer; on the other hand, PD was expected to increase the hydrophilicity of PES support layer for being more easily wetted by aqueous amine solution to facilitate interfacial polymerization. The TFC membranes were characterized by scanning electron microscopic (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), zeta potential measurement and water contact angle measurement. The separation performance of the membranes was evaluated by the filtration of inorganic salts and the measurement of molecular weight cut-off (MWCO) using PEGs. The structure stability of the resultant membrane was investigated in detail.

## 2. Experimental section

### 2.1. Materials

Polyethersulfone (PES, E6020P,  $M_w=59,000$ ) was purchased from BASF Co. (Germany) and dried at 110 °C for 12 h before use. Poly (ethylene glycol) (PEG,  $M_w=200, 400, 600, 1000, 2000$ ), N, N-dimethylformamide (DMF), n-heptane, ethanol and hydrochloric acid (HCl) were purchased from Kewei Chemical Reagent Co. (Tianjin, China). Trimesoyl chloride (TMC) was purchased from Alfa Co. (USA). Dopamine hydrochloride was purchased from Yuancheng Technology Development Co. (Wuhan, China). Tris (hydroxymethyl) aminomethane (Tris) was purchased from Sigma-Aldrich (Canada).

Piperazine (PIP),  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , NaCl and  $\text{MgCl}_2$  were received from Guangfu Fine Chemical Research Institute (Tianjin, China). The water used was deionized water at pH 6.0.

### 2.2. Preparation of the TFC membrane

PES ultrafiltration membranes modified by PD were used as the support layer of TFC membrane. The fabrication of PES ultrafiltration membranes with PEG2000 as pore forming agent have been described in our previous works [46]. Pure water flux of the PES membrane was about 160 L/( $\text{m}^2$  h) under 0.1 MPa, and the bovine serum albumin (BSA, 67 kDa) rejection of the PES membrane was about 98%. In the dopamine coating process, circular pieces of PES membrane were soaked in the dopamine solution (2.0 g/L) and shaken in a shaking water bath with speed 200 rpm at 25 °C for 30 min. Tris-HCl solution (50 mM, pH 8.5) was chosen as buffer solution according to previous research [26,47]. Then the modified PES membrane as support layer, named PD-PES membrane, was taken out and thoroughly washed with deionized water to remove most residual unbound polydopamine. After the coating, the PD-PES membrane was firstly immersed into aqueous solution of PIP at 50 °C for 30 min. Then PIP impregnated membrane, named PIP/PD-PES membrane, was taken out from PIP solution and the excess water was drained off in the air. The organic phase prepared by dissolving TMC in n-hexane was subsequently introduced to cover the surface of PIP impregnated membrane for a certain time, forming a polyamide layer over the surface of PD-PES membrane through interfacial polymerization. Afterwards, the resultant TFC membrane (PA/PD-PES) was air dried for 30 min to allow the n-heptane to evaporate and subsequently post-treated for attaining the desired stability of the formed structure. Finally, the resultant membrane was rinsed with deionized water and kept in deionized water before carrying out evaluation studies. The TFC membrane using unmodified PES membrane as support layer was also prepared as the control membrane, named PA/PES membrane.

### 2.3. Characterization of the TFC membrane

The cross sectional and surface morphologies of the TFC membranes were observed by SEM using a NanoSEM 430 scanning microscope. The membrane samples frozen in liquid nitrogen were broken and sputtered with gold before SEM analysis. The hydrophilicity of PES, PD-PES, PIP/PD-PES, PA/PES and PA/PD-PES membranes surface was determined by conducting the static contact angle measurement with contact angle goniometer (JC2000C, Shanghai, China) at room temperature. At least five contact angles at different locations on one surface were averaged to get a reliable value. FT-IR spectra of PES, PD-PES, PA/PES and PA/PD-PES membranes were recorded using a Nicolet 6700 spectrometer (Thermo Nicolet, USA) with the scan range of 4000–500  $\text{cm}^{-1}$  and the resolution of 2  $\text{cm}^{-1}$ . The experiments were performed using air as the background and all the spectra were baseline corrected. The surface composition of the membranes were analyzed by XPS (Kratos Axis Ultra DLD) using Al  $K\alpha$  (1486.6 eV) as the radiation source. All XPS spectra were recorded using an aperture slot of 300 × 700  $\mu\text{m}$ , and survey spectra were collected over a range of 0–1100 eV. The takeoff angle of the photoelectron was set at 90°, corresponding to the measured depths of about 10 nm. The zeta potential was determined from streaming potential measurements by Electro Kinetic Analyzer (Austria/Anton Paar KG, Austria) equipped with a plated sample cell. The measurements were carried out using a 1 mM KCl solution in the range of pH 2–10 at 25 ± 0.5 °C. The resultant zeta potential was calculated using the Helmholtz–Smoluchowski equation.

Download English Version:

<https://daneshyari.com/en/article/7021544>

Download Persian Version:

<https://daneshyari.com/article/7021544>

[Daneshyari.com](https://daneshyari.com)