



Novel nanofiltration membrane with ultrathin zirconia film as selective layer



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ABSTRACT

Thin film composite (TFC) membranes with ultrathin dense selective layer have emerged as a promising candidate for nanofiltration with excellent permeation and rejection performance. Herein, novel organic–inorganic TFC nanofiltration membranes (TFC NFMs) are fabricated via the mussel-inspired modification of ultrafiltration membrane followed by a mineralization process. Hydrolyzed polyacrylonitrile (HPAN) ultrafiltration membrane is facilely co-deposited with polydopamine (PDA) and polyethylenimine (PEI), and the PDA-PEI coating further induces the growth of zirconia (ZrO₂) nanoparticles on the membrane surface. The formed zirconia selective layer is defect-free, uniform, and ultrathin (10–20 nm). The organic–inorganic TFC NFMs show high retention (> 90%) for bivalent cations with a salts rejection sequence of MgCl₂ > CaCl₂ > MgSO₄ > NaCl > Na₂SO₄ at pH 6.0 ascribed to the positively charged membrane surface. The water flux reaches as high as 60 L/m² h under 0.6 MPa due to the ultrathin and hydrophilic properties of the inorganic selective layer. Moreover, the organic–inorganic TFC NFMs show good structure stability for long-term nanofiltration operation.

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1. Introduction

The extended drought and water pollution have become one of the most pervasive environmental issues in the worldwide, which is calling for novel materials and approaches to water purification and reuse [1,2]. During the last decades, nanofiltration has emerged as an efficient process for drinking water production and wastewater treatment. It exhibits great advantages of low operation pressure, high permeation flux, superior retention of multivalent ions and organic molecular (200–1000 Da) along with reduced investment, operation and maintenance costs [3,4]. Nanofiltration membranes (NFMs) are the core of nanofiltration processes for water purification, which can be categorized into organic polymer membranes and inorganic ceramic ones. In general, good flexibility, low cost and small footprint are the major merits of polymer NFMs. However, polymer NFMs are of relatively low

chemical, structural and thermal stability with surface fouling and limited lifespan [5]. By contrast, inorganic NFMs possess the benefits of good thermal and chemical stability, high mechanical strength, outstanding hydrophilicity and long lifetime along with drawbacks of complicated and expensive fabrication process and fragile structures [6]. The organic–inorganic composite NFMs provide a promising access to overcome these disadvantages by combining the superiorities of the two categories of membranes. However, it remains a major challenge to achieve such NFMs with ideal structures and high performance to date [7].

Generally, most of the ideal NFMs are thin film composite (TFC) membranes with a support and a thin selective layer. Organic–inorganic TFC NFMs have usually been fabricated by dispersing inorganic fillers in the polymer selective layer through blending, in-situ formation or sol–gel method [8–12]. Though the performance is improved as compared with typical polymer or ceramic membranes, thickness of the selective layer is difficult to be reduced and the properties of the inorganic fillers are concealed by the polymer matrix. Moreover, poor compatibility of the organic polymers with the inorganic fillers presents the most challenge in the fabrication of TFC NFMs with high performance, which often leads to defective voids and low stability in the selective top layer [9,13–15]. It may be an avenue to fabricate TFC NFMs with an ultrathin inorganic top layer on the polymeric substrate. Few explorations have been conducted, for example, self-assembly of inorganic nanoparticles on the membrane surfaces [16,17]. It is

Abbreviations: NFMs, Nanofiltration membranes; TFC, thin film composite; PDA, polydopamine; PEI, polyethylenimine; ZrO₂, zirconia; HPAN, hydrolyzed polyacrylonitrile; FT-IR/ATR, attenuated total reflectance Fourier transform infrared spectrometer; XPS, X-ray photoelectron spectrometer; FESEM, Field emission scanning electron microscopy; EDX, energy dispersive X-ray spectroscopy; XRD, X-ray diffraction; AFM, atom force microscopy; F_w, water flux; R, rejection; WCA, water contact angle

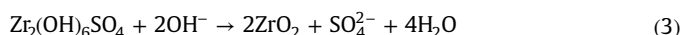
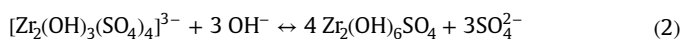
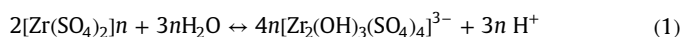
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reasonable to recognize that the assembly density, uniformity and stability of the inorganic layer leave much to be desirable for robust TFC NFMs.

Dopamine, a well-known “bio-glue”, can be oxidized in alkaline environment and forms a polymer-like coating on various substrates with great adhesive strength [18–21]. Numerous of studies have applied this mussel-inspired coating for membrane preparation such as surface modification, functionalization and top layer fabrication [22–26]. The polydopamine (PDA) coating can further act as a bridge to chelate with certain metal oxides for constructing inorganic films on various substrates [27–31]. This “bio-glue” effect provides excellent interfacial stability between the polymer substrate and the inorganic layer. Nevertheless, the self-aggregation of PDA always leads to particle-like morphology, which is not favorable to fabricate a smooth and dense selective layer. In our previous work, low-molecular-weight polyethylenimine (PEI) was used as a cross-linking component to promote the homogeneous polymerization of dopamine and the uniform co-deposition of PDA-PEI without PDA self-aggregation [25,32,33]. Simultaneously, the PDA-PEI intermediate coating provides a coordination force to induce subsequent mineralization of inorganic nanoparticles and to stabilize the formed inorganic layer on the membrane surfaces [29–31]. Additionally, the chelation between PDA-PEI coating and metal ion suppresses the mineralization process during hydrolysis reaction and thus results in ultrafine nanoparticles [11]. These characteristics are favorable for constructing TFC NFMs with defect-free ultrathin selective layer.

Herein, we report a novel type of organic–inorganic TFC NFMs with an ultrathin inorganic selective layer on PDA-PEI coated polyacrylonitrile ultrafiltration membranes via a coordination-driven deposition process (Fig. 1). Zirconia (ZrO_2) was adopted as the inorganic selective layer because it has been widely used for high performance filtration membranes as an inorganic component with superior chemical, physical and thermal stability and good hydrophilicity [27,29]. The ultrathin ZrO_2 layer can be resulted from the controlled hydrolysis process of zirconium sulfate. The equilibrium reactions are listed as follows [27,34,35]:



In our cases, the ultrathin ZrO_2 selective layer endows the TFC NFMs with relatively high water flux (over $60 L/m^2 h$ under 0.6 MPa) accompanied by high rejection performance ($> 90\%$) for multivalent cations. Furthermore, the TFC NFMs even show robust structure stability for long-term operation.

2. Experimental

2.1. Materials

Polyacrylonitrile ultrafiltration membrane (MWCO ranging from 10 to 300 kDa) is commercial product of Shanghai MegaVision Membrane Engineering & Technology Co. Ltd (China). Dopamine hydrochloride and PEI ($M_w=600$ Da) were purchased from Sigma-Aldrich (USA) and Aladdin (China), respectively. Zirconium sulfate tetrahydrate, tris(hydroxymethyl) aminomethane, ethanol, sodium hydroxide, and hydrochloric acid solution (12 mol/L) were all obtained from Sinopharm Chemical Reagent Co., Ltd and used as received.

2.2. Preparation of the organic–inorganic TFC NFMs

The fabrication process is schematically presented in Fig. 1. Polyacrylonitrile ultrafiltration membrane was hydrolyzed in sodium hydroxide solution (1.5 mol/L) for 1 h at 50 °C, and then immersed into hydrochloric acid solution (2 mol/L) for another 1 h at 25 °C before use. Dopamine hydrochloride and PEI were dissolved in Tris–HCl buffer solution (pH=8.5, 50 mmol/L) to prepare fresh solution for deposition. The mass ratio was fixed at 1:1 with a total concentration of 2 mg/mL and the deposition time was chosen as 2 h according to our previous work [32]. These conditions are based on the mass of PDA-PEI deposited on the membrane surface and the thickness of the coating layer. The circular pieces of HPAN membrane with diameter of 40 mm were pre-wetted by ethanol for 30 min, and then transferred into the freshly prepared dopamine/PEI solution and shaken at 25 °C for 2 h. The as-prepared mussel-inspired platforms (PDA-PEI coated HPAN membranes) were washed by deionized water for several times and dried in ambient environment. Zirconium sulfate tetrahydrate was dissolved in hydrochloric solution (40 mmol/L) with a concentration of 4 mmol/L. Subsequently, the PDA-PEI coated HPAN membranes were immersed into the solution at room temperature (25 °C) for 12 h. Finally, the resulted organic–inorganic TFC NFMs were rinsed several times and dried in vacuum oven over night for further characterization and evaluation.

2.3. Membrane characterization

The chemical structures and detailed components of the membrane surfaces were analyzed by attenuated total reflectance Fourier transform infrared spectrometer (FT-IR/ATR, Nicolet 6700, USA) and X-ray photoelectron spectrometer (XPS, Thermo-Scientific, USA) with argon-ion etching (3000 eV, mid current), respectively. The X-ray diffraction (XRD, Ultima IV, Japan) was used to determine the phase state of ZrO_2 film. Field emission scanning electron microscopy (FESEM) and energy dispersive

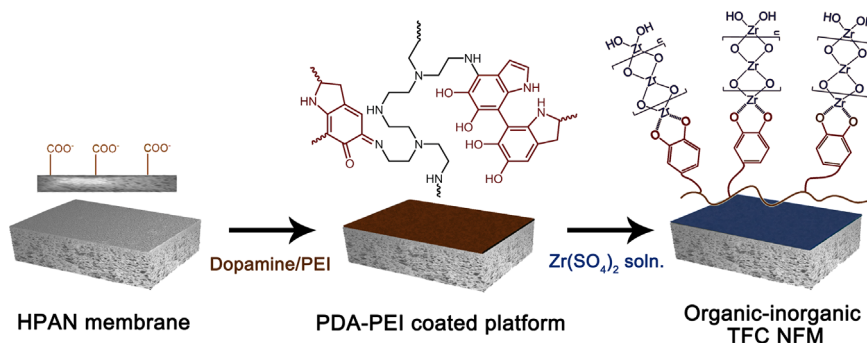


Fig. 1. Schematic diagram of the preparation process and mechanism for the organic–inorganic TFC NFMs with ultrathin ZrO_2 film as the selective layer on the PDA-PEI coated polyacrylonitrile membranes.

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