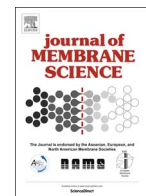




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journal homepage: www.elsevier.com/locate/memsciElevating the selectivity of layer-by-layer membranes by *in situ* bioinspired mineralizationGuanhua Liu^{a,b}, Zhongyi Jiang^{a,b}, Xuanxuan Cheng^{a,b}, Cheng Chen^{a,b}, Hao Yang^{a,b}, Hong Wu^{a,b}, Fusheng Pan^{a,b,*}, Peng Zhang^{c,d}, Xingzhong Cao^{c,d}^a Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China^b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China^c Multi-discipline Research Division, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China^d Beijing Engineering Research Center of Radiographic Techniques and Equipment, Beijing 100049, China

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ABSTRACT

Layer-by-layer (LbL) assembly is a common method for controlled fabrication of ultrathin membranes, while bioinspired mineralization is a novel method for controlled synthesis of well-dispersed inorganic particles in hybrid membranes. Here, bioinspired mineralization was integrated with LbL assembly to prepare ultrathin polymer-inorganic hybrid membranes by *in situ* precipitating silica nanoparticles into alternatively assembled polyethyleneimine (PEI) and sodium alginate (Alg). The membrane thickness was manipulated by varying the bilayer numbers. And the synthesized silica nanoparticles were revealed by the surface morphology, Si mapping and chemical properties of the membranes. The surface hydrophilicity, diffusion selectivity and the fractional free volume of the hybrid membranes were all enhanced by the incorporation of silica nanoparticles. As a result, the ultrathin hybrid membrane showed elevated selectivity (2.66-fold higher than that of control membrane) with almost unchanged permeability when used for pervaporation dehydration of 90 wt% ethanol aqueous solution as a model mixture. This study indicates the great potential for overcoming the tradeoff hurdle between permeability and selectivity by the synergy of LbL assembly and bioinspired mineralization to fabricate ultrathin hybrid membranes.

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1. Introduction

Membrane technologies have drawn increasing attention in commercial separation applications due to the inherent advantages of easy scale-up, high efficiency and low environmental impact [1]. The design and fabrication of membrane materials play a dominant role in improving their performance. Till now, a wide range of methods (such as phase inversion, surface coating, layer-by-layer (LbL) assembly, co-extrusion spinning, thin film polymerization, etc.) have been used for membrane fabrication [2–4]. Among them, LbL assembly has experienced considerable growth due to the nanoscale control of membrane thickness, the large varieties of membrane materials, and the flexible manipulation of interfacial interactions. Generally, the thin membrane would

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benefit the permeability but is unfavorable to a high selectivity [5,6]. On the other hand, hybrid membranes by incorporating inorganic fillers into polymer matrix have been demonstrated to be a facile and efficient approach to increase permeability and selectivity simultaneously and thus to overcome the inherent tradeoff effect of polymer membranes [7]. The physical and chemical properties of fillers endow membranes with appropriate free volume characteristics and additional polymer-filler interfaces, thus increasing the selectivity [8,9]. Till now, many types of fillers (such as silica [10], metal oxide [11], clay [12], graphene oxide [13], metal-organic framework (MOF) [14] and carbon nanotube (CNT) [15]) have been used and shown encouraging outcome in elevating the membrane performance. But the hybrid membranes are difficult to be fabricated as ultrathin membranes in conventional ways, which often leads to too low permeation flux to meet the practical application requirement.

Presently, one feasible solution is to fabricate hybrid membranes by LbL assembly method in order to merge the advantages of LbL membranes and hybrid membranes. The incorporation of

fillers is mainly focused on physical blending and *in situ* methods [16]. To avoid structural voids, the membrane thickness needs to be more than 10 times as that of fillers [17]. And the thickness of LbL membranes is generally lower than 300 nm, so the size of fillers is expected to be smaller than 30 nm. Fillers at this scale tend to severely aggregate in physical blending method, which makes it difficult to fabricate ultrathin membranes [16,18,19]. As for *in situ* method, the nano-sized fillers are generated within the polymer matrix, which creates well-distributed fillers and uniform filler-polymer interfaces [20]. Several efforts (including sol-gel method [21,22], coordination reaction method [19,23] and bioinspired mineralization method [24]) have recently been devoted to incorporating inorganic fillers in polymer membranes for diverse separations.

Among these *in situ* methods, bioinspired mineralization has emerged as a novel and promising method to synthesize inorganic materials in confined space [3]. Biomineralization refers to the natural process, by which living organism (such as diatoms, mollusks, etc.) generates varied biominerals from soluble compounds. Through mimicking the biomineralization process, bioinspired mineralization represents an artificial process, by which inorganic minerals are synthesized utilizing the mechanisms involved in the formation of biominerals [25]. Bioinspired mineralization takes place at room temperature, atmospheric pressure and nearly neutral pH conditions. These inorganic materials are composed of inorganic phase and biopolymer thus compatible with polymer, and synthesized *in situ* onto specific sites of organic inducers [26]. In our previous studies, silica nanoparticles have been synthesized in polymer membranes with good dispersion and interfacial compatibility for separation processes [27,28]. In other literature, bioinspired mineralization has been used to tune the membrane structure [24], the membrane surface hydrophilicity and charge property for enhanced separation performance [29,30]. Therefore, it is attractive to employ the polymer moiety within LbL membranes as the mineralization inducer to *in situ* synthesize fillers. It should be mentioned that it is rarely reported to combine bioinspired mineralization with LbL assembly for overcoming the tradeoff hurdle of separation membranes. To be specific, long-chain macromolecules (such as polyamines and polycationic polypeptides) could serve as building blocks for LbL assembly process, and then act as mineralization inducers to precipitate the inorganic precursors around the active charges [31,32].

In this study, polyethyleneimine (PEI) and sodium alginate (Alg) were used as polyelectrolytes to form LbL membranes through electrostatic interaction on hydrolyzed polyacrylonitrile (HPAN) ultrafiltration membranes. Meanwhile, sodium silicate was used as inorganic precursor and mineralized by the mediation of PEI. The LbL assembly processes were verified by surface zeta potential. The morphology, physical and chemical properties, and hydrophilicity of the membrane were extensively tested. The separation performance of the resulting ultrathin hybrid membranes was evaluated with 90 wt% ethanol aqueous solution as a model mixture. The influence of operating temperature on the separation performance of membranes was also investigated.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN) flat-sheet ultrafiltration membranes with molecular weight cut-off of 100,000 were used as membrane substrates and bought from Shanghai MegaVision Membrane Engineering and Technology Co. Ltd. (Shanghai, China). Sodium alginate was supplied by Qingdao Bright Moon Seaweed Group Co. Ltd. (Shandong, China). Polyethyleneimine (MW 750,000) was

purchased from Sigma-Aldrich (USA). Hydrochloric acid (HCl, 36–38 wt%) was bought from Tianjin Kewei Ltd (Tianjin, China). Sodium hydroxide (NaOH), sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) and absolute ethanol were supplied by Tianjin Guangfu Technology Development Co. Ltd. (Tianjin, China).

All the reagents were of analytical grade and used without further purification. Deionized water from a Millipore system (Milli-Q[®]) was used through the experiments.

2.2. Preparation of PEI/Alg-Si ultrathin hybrid membranes

The PAN flat-sheet ultrafiltration membranes were immersed in water for two days to remove glycerol, treated with NaOH aqueous solution (1.5 mol/L) at 55 °C for 30 min, and then washed with water to neutral pH. The acquired hydrolyzed PAN (HPAN) membranes were dried at room temperature before use. Alg was dissolved in water under stirring with a concentration of 2 mg/mL at 30 °C, after which a certain amount of Na_2SiO_3 was added in the solution and then acidified to pH 8.0 using 0.5 M HCl solution to prepare Alg/ Na_2SiO_3 solution. PEI aqueous solution (2 mg/mL) was prepared and acidified to pH 8.0 using 0.5 M HCl solution.

The following steps were employed for alternative deposition of Alg/ Na_2SiO_3 and PEI. (a) PEI solution was spin-coated onto HPAN substrate at 1500 rpm for 20 s (b) The membrane was rinsed with water for three times. (c) Alg/ Na_2SiO_3 solution was spin-coated onto the membrane in step (b) at 1500 rpm for 20 s (d) The membrane was rinsed with water for three times. (e) Steps (a–d) were repeated for certain times. The resultant membranes were dried at room temperature. For simplicity, the membranes were denoted as (PEI/Alg-Si(X))_Y, where X represented the concentration of Na_2SiO_3 in Alg/ Na_2SiO_3 solution (mM), ranging from 2.5 to 10, and Y represented the bilayer numbers of the membranes, ranging from 0.5 to 10. Thereinto, (PEI/Alg-Si(X))_{0.5} represented the membrane with just one PEI layer. For comparison, (PEI/Alg)_Y membrane was prepared. Accordingly, no Na_2SiO_3 was added in the Alg solution, which was alkalified to pH 8.0 using 0.5 M NaOH solution. PEI/Alg-Si(X) complexes were prepared by blending the solution of PEI with Alg/ Na_2SiO_3 solution.

2.3. Characterizations

The surface morphology (after conductive coating with gold) and cross-section morphology (after freeze fracturing with liquid nitrogen and conductive coating with gold) of the LbL membranes were observed by field emission scanning electron microscope (FESEM, Nanosem 430). The silicon distribution was measured by energy-dispersive X-ray spectroscopy (EDX) coupled with FESEM. The surface morphologies of membranes were scanned by atomic force microscope (AFM, Bruker Dimension Icon system). The chemical properties of membranes were recorded on a Fourier transform infrared spectra in the range of 4000–500 cm^{-1} (FT-IR, BRUKER Vertex 70). Thermogravimetric analysis (TGA, NETZSCH TG 209 F3) of PEI/Alg-Si(X) complexes was performed with a heating rate of 10 °C/min in the range of 40–800 °C under an oxygen atmosphere. The surface zeta potential of the LbL membranes was measured through tangential flow streaming potential method via an electrokinetic analyzer (Anton Paar GmbH, Austria) in 1 mM KCl solution (pH=7.0 ± 0.2). Zeta potential values were calculated using the Helmholtz–Smoluchowski equation. The static contact angles of membranes were measured by JCL2000D Contact Angle Meter, and the data were acquired by at least 8 different sites on the membranes. The free volume properties of the membranes were characterized by the positron annihilation technology. The slow positrons emitting from ²²Na source annihilated in the membrane and released γ photons, which revealed the information of cavities at the annihilation position. The

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