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Mineralization-inspired preparation of composite membranes with polyethyleneimine–nanoparticle hybrid active layer for solvent resistant nanofiltration

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ABSTRACT

Inspired by mineralization, a series of composite membranes with polymer–nanoparticle hybrid active layer were prepared via a generic and facile approach in this study for solvent resistant nanofiltration. Polyethyleneimine (PEI) was employed as polymer matrix, the $-NH_2$/–NH– groups of which catalyzed the inorganic precursor (tetraethoxysilane/tetra-n-butyl titanate) to synthesize inorganic nanoparticles (silica/titania) with tunable structure. Then, the active layers were covalently cross-linked for further enhancing the thermal and structural stabilities of the composite membranes. The composition and microstructure of the composite membranes were investigated through Fourier transform infrared spectroscopy, scanning electron microscope, thermogravimetric analysis, and contact angle measurement. The nanofiltration performances in terms of solvent uptake, area swelling, flux, and rejection of the composite membranes were measured using n-heptane, toluene, butanone, ethyl acetate, and isopropanol as solvents, as well as polyethylene glycol as solute. The results suggested that the presence of nanoparticles in active layer endowed the composite membrane with excellent solvent resistance in the above solvents (area swelling below 6%). Meanwhile, the nanoparticles dramatically elevated the rejection of the composite membrane while remaining the sufficient solvent flux and promising long-term operation stability. Moreover, the influence of the type of nanoparticle on the membrane performances was evaluated in detail.

1. Introduction

As a new burgeoning technology, solvent resistant nanofiltration (SRNF) is an energy- and waste-efficient unit process that allows the separation of organic mixtures by simply applying a pressure gradient through a membrane [1–3]. SRNF has been applied in oil refining, catalysis, food and pharmaceutical industries [4–7]. The development of SRNF membrane, which possesses high rejection and acceptable solvent flux in a wide range of organic solvents, remains a daunting challenge and has attracted increasing attention. The commercial SRNF membranes are mainly fabricated using polydimethylsiloxane (PDMS) and polyimides (PI). After cross-linking, the PDMS and PI present excellent solvent resistance, good mechanical and thermal stabilities [8,9]. PDMS-based membranes are found to be applied to polar solvents with sufficient solvent flux and solute rejection. However, PDMS, as an elastomer, tends to swell or dissolve via solvation effect in non-polar solvents, leading to elevated solvent flux but compromised rejection [10,11]. While, the PI-based membranes usually had low permeate flux for non-polar solvents, due to the weak interactions between the active layer and non-polar solvent molecules.

The nanofiltration performances of SRNF membranes have been demonstrated to be dependent on the membrane structure and the inherent chain packing of polymer matrix [12]. Accordingly, abundant studies have been dedicated to adjusting the physico-chemical properties of PDMS-based and PI-based membranes to rectify the trade-off between flux and rejection. Among the various approaches, cross-linking and hybridization have been examined to be two facile and efficient ways [13–15]. The former can construct toughly multidimensional networks to suppress the chain mobility through chemical reaction. The latter can regulate the free volume characteristics and chain packing of polymer matrix via interfacial interaction. Through these manners, the

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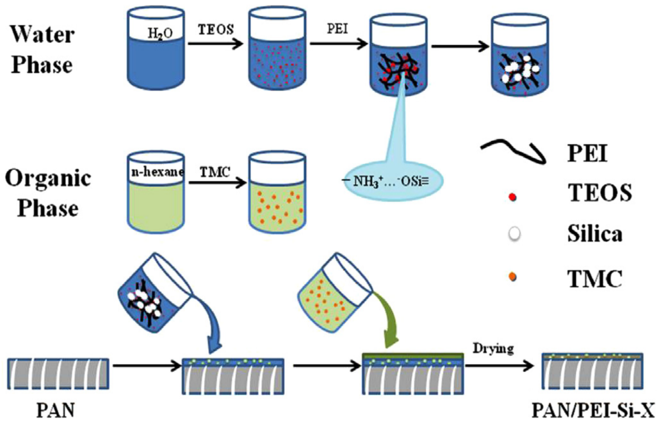
solvent resistance and nanofiltration performances of the SRNF membrane can be tailored efficiently.

Despite the superior advantages of hybridization, the up-scaling preparation of composite membrane with defect-free hybrid active layer is still not straightforward. Besides, the hybrid active layer always suffers from severe aggregation of inorganic nanoparticles due to their high surface area and poor interfacial compatibility with polymer matrix [16]. Consequently, non-selective voids are generated among the interfacial domains, which will cause low rejection. To obtain adequate rejection, thicker active layers (at least several times of the size of the fillers) have been utilized in many literatures. However, the resulting membranes usually have low solvent flux due to the decrease of diffusion coefficient [17–19]. Recently, inspired by the mechanism of mineralization, organic–inorganic hybrid membranes have been prepared via a facile approach. Basic polymer bearing amine groups was utilized as membrane matrix, the amine groups of which meanwhile acted as catalyst to generate inorganic nanoparticles through the hydrolysis and condensation of inorganic precursors [20–22]. Through this in situ process, inorganic nanoparticles with size uniformity and tunability are generated within the polymer matrix under mild conditions [23]. The formation of non-selective voids can be eliminated due to the good compatibility between the polymer and nanoparticles. Attracted by these advantages, this method has been employed to prepare hybrid membranes for the applications of pervaporation and gas separation. Jiang et al. developed a series of composite membranes with hybrid skin layers (e.g., polyvinyl alcohol–silica and gelatin–silica) inspired by mineralization, which achieved enhanced permeation flux and desired separation factor for propylene gas dehumidification and model gasoline separation [24,25]. Despite the unique advantages and common applications, this method has seldom been reported in the preparation of SRNF membrane.

Currently, polyethylenimine (PEI) has been discovered as a generic membrane material for ultra-filtration and solvent resistant nanofiltration [26–29], owing to its high temperature durability, excellent mechanical and chemical properties. Meanwhile, the abundant amine groups in PEI chains exert the function of mineralization to create PEI-nanoparticle nanostructure [30–32]. During this process, the PEI chains work as template and achieve well compatible polymer–inorganic structures without aggregation. In addition, the structural stability of PEI-based membranes can be facilely enhanced by cross-linking [33].

In this study, a series of composite membranes with defect-free hybrid active layer were prepared inspired by mineralization and then cross-linked for SRNF application for the first time. The facile preparation approach would provide uniformly dispersed inorganic nanoparticles (silica/titania) with tunable structure in the active layers of composite membranes. Hydrolyzed polyacrylonitrile (PAN) was chosen as the support. The microstructures and physicochemical properties of the as-prepared membranes were regulated by the kind and loading amount of inorganic precursor. The SRNF performances in terms of solvent uptake, area swelling, flux, and rejection of the composite membranes in both polar and non-polar solvents were investigated in detail.



Scheme 1. Synthesis process of the PAN/PEI–Si–X.

2. Experimental

2.1. Materials

PEI (*Mw* 20,000 Da), trimesoyl chloride (TMC), and tetraethoxysilane (TEOS) were purchased from Alfa Aesar without any further purification. PAN support with molecular weight cut-off (MWCO) of 100 kDa was purchased from Shanghai MegaVision Membrane Engineering & Technology Co., Ltd, which was hydrolyzed before utilization. Polyethylene glycol (PEG, *Mw* of 200, 400, 600, 800, 1000, and 2000) oligomers and tetra-n-butyl titanate (TBOT) were provided by Chengdu Xiya Reagent Research Center. Isopropanol, hexane, n-heptane, and ethyl acetate were obtained from Tianjin Kermel Chemistry Co., Ltd. Toluene, butanone, and sodium hydroxide were supplied by Guangfu Fine Chemical Research Institute. De-ionized water was used throughout the experiment.

2.2. Preparation of the composite membranes

Prior to the preparation of composite membrane, the PAN support was first tailored into disc with the diameter of 9 cm. Then, the disc was immersed in NaOH solution (1 M) at 50 °C for 1 h. The residual NaOH was removed by washing with water until the pH of the rinsed water reached about 7.0. Finally, the hydrolyzed PAN support was stored in water for its subsequent use.

The synthesis strategy of PEI–silica composite membrane was shown in Scheme 1. Prior to casting, the PAN support was immersed in water to reduce the intrusion of PEI molecules into the pores of PAN. A certain amount of TEOS was dispersed in water by ultrasonic agitation in an ice-water bath. PEI (2.0 g) was dissolved into the above solution (4 wt%, 50 mL) under stirring. It was found that the pH value of the mixed solution was 7.6. Then, the obtained solution was dip-coated onto the upper surface of PAN support for 10 min at 25 °C to obtain a thin and defect-free PEI layer. Afterwards, the TMC (2 wt%, 50 mL) hexane solution was prepared under mechanical stirring for 1 h and then cast onto the coated PAN support for another 10 min at 25 °C to perform the cross-linking reaction. Then, the resulting composite membrane was dried for 15 min in air, and then in a drying cabinet for 12 h at 60 °C to make the residual hexane evaporate and the cross-linking reaction complete.

Similarly, the PEI–titania composite membranes were prepared through the same procedure as that of PEI–silica composite membranes but using TBOT as inorganic precursor. For comparison, the PAN/PEI was fabricated in exactly the same way without incorporating inorganic precursor. All the obtained membranes were dried completely prior to utilization. The namings of the composite membranes were listed in Table 1, in which PAN/PEI–Si–*X* or PAN/PEI–Ti–*X* represented silica or titania nanoparticles as the fillers, where *X* (*X*=0.2, 0.4, 0.6, or 0.8) represented the weight percentage (wt%) of the inorganic precursor to PEI.