

Thin film nanocomposite membranes based on imogolite nanotubes blended substrates for forward osmosis desalination



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ARTICLE INFO

Keywords:

Imogolite nanotube
Forward osmosis membranes
Structural parameter
Internal concentration polarization
Desalination

ABSTRACT

Novel thin film nanocomposite (TFN) membranes were fabricated by interfacial polymerization on imogolite nanotubes (INTs) blended substrates for the forward osmosis (FO) desalination. INTs as intrinsically hydrophilic nanotubes were synthesized and characterized to be with length of 100–200 nm, outer diameter of 2 nm, and inner diameter of 1 nm. Then, different INTs loading (0.33, 0.66 and 1.0 wt%) were used to prepare INTs blended polysulfone (PSf) substrates, whose morphology and properties were investigated in detail. It is found that the incorporation of INTs obviously enhanced the hydrophilicity, pure water flux, overall porosity, surface porosity and roughness of PSf substrates. The TFN membranes demonstrated superior water permeance and salt rejection compared to the thin film composite (TFC) membranes. Among others, TFN 0.66 with 0.66 wt% INTs blended PSf substrate showed the best over-all properties which are important for demonstrating good osmotic performance in FO. Moreover, TFN membranes presented smaller structural parameters than TFC membrane, which means that internal concentration polarization (ICP) effect can be alleviated by incorporating hydrophilic INTs into substrates. The obtained TFN membranes with INTs blended substrates could develop opportunities in desalination.

1. Introduction

Forward osmosis (FO) has attracted extensive attention as a promising platform for available desalination and sustainable power generation [1–3]. This process exploits a selective semi-permeable membrane separating a feed solution (low osmotic pressure) and a draw solution (high osmotic pressure). Based on their osmotic pressure difference, water can be driven across the semi-permeable membrane from the feed solution to the draw side. Since no external pressure is applied, FO benefits from low energy consumption and long membrane lifetime with acceptable fouling resistance compared to conventional pressure driven membrane processes [2]. Even so, it is a crucial challenge to design and fabricate a semi-permeable membrane with good osmotic performance and low fouling to effectively implement FO process.

In the last decade, thin film composite (TFC) membranes have been known to be the most efficient FO membranes, possessing the ease to optimize membrane substrates and active layers separately [4,5]. However, the difficult solute diffusion through the porous substrates mainly results in severe internal concentration polarization (ICP), which is the prominent factor reducing the net driving force and

causing poor water flux for FO membranes [3]. It is found that the effect of ICP can be alleviated by minimizing the structural parameter (S) of the membrane substrates. The S parameter proportionally decreases as the porosity increases, while increases with the thickness and tortuosity of the substrates [6]. Moreover, ICP can be reduced by using a hydrophilic substrate without greatly sacrificing strength or flexibility [7]. That is because a hydrophilic substrate with improved wettability not only facilitates the transport of water and solute molecules, but also decreases the effective tortuosity and increases the effective porosity to reduce the air entrapping in the membrane pores.

Nanotechnology explores attractive options and solutions to reduce structural parameter [8], enhance hydrophilicity [7], and improve mechanical strength [9] by incorporating inorganic nanoparticles into the substrates of TFC membranes to form thin film nanocomposite (TFN) membranes [10]. According to the dimensional nanoscale, the inorganic nanoparticles can be classified into 0D (TiO₂ [11], Al₂O₃ [12], SiO₂ [13], Ag [14], etc.), 1D (CNTs [15], TiO₂ nanotube [16], et al.), 2D (graphene [17], graphene oxide [4], clay silicate [18], etc.) and 3D (zeolite [19], metal organic framework [20], etc.). Among others, 1D nanoparticles exhibit vast potentials in desalination applications owing to their unique tubular structure providing diffusion paths

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as well as 1D single-file ordering for fast mass transfer of water molecules. For example, CNTs with diameter of 1–2 nm are considered to be good candidates for the next generation of water desalination membranes based on their spontaneous filling and fast conduction of water through the 1D nanotubes [21,22]. Wang et al. [23] added 2 wt% carboxylated MWCNTs into polyethersulfone (PES) substrate to form TFN membrane, whose water flux was higher than that of TFC membrane with neat PES substrate. Amini et al. [24] proposed that TFN membranes containing 0.1 wt% MWCNTs functionalized with amine groups showed a water flux 160% higher than TFC membrane. However, the addition of the pristine CNTs always displays weak or even no effects on the improvement of water permeability of FO membranes due to their intrinsic hydrophobicity [25]. It is required to sophisticated functionalization and post-synthesis for the pristine CNTs before introduced to TFN membranes. Therefore, it should be much easy and effective to directly incorporate hydrophilic 1D nanoparticle without pretreatment.

In fact, several inorganic metal oxide nanotubes with hydrophilicity have been reported to open new routes toward TFN membranes for FO process [8]. Imogolite nanotubes (INTs) have emerged as one of the most promising competitors of CNTs in some areas of nanosciences. They are a kind of single-walled nanotube materials consisting of hydrous aluminosilicate, and having the general formula of $(\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH}$ [26]. Contrarily to CNTs, INTs benefit from their outstanding hydrophilicity based on the abundant hydroxyl groups both on their inner and outer walls (Fig. 1). This feature may regard incorporating imogolite into polymer matrix as a feasible way to promote the hydrophilicity of membranes [27]. Furthermore, INTs have high surface area and aspect ratio with length running from a few tens to several hundreds of nanometers, and inner and outer diameters of 1 and 2 nm, respectively. These physicochemical properties provide imogolite huge potential applications in desalination [28].

We explore herein the possibility to fabricate a novel TFN membrane for FO processes by incorporating the hydrophilic INTs into the substrates. In this paper, INTs were synthesized to be with length of 100–200 nm, outer diameter of 2 nm, and inner diameter of 1 nm. Detailed investigation has been focused on the effects of the hydrophilic INTs on the properties and morphology of substrates and TFN membranes. Moreover, we also discussed the influence of INTs on ICP, structural parameter, water permeability and salt rejection of TFN membranes. The obtained TFN membranes with INTs blended substrates could develop opportunities in desalination and power generation.

2. Experimental

2.1. Materials

Polysulfone (PSf, $M_n = 22,000$) were purchased from Solvay Co.,

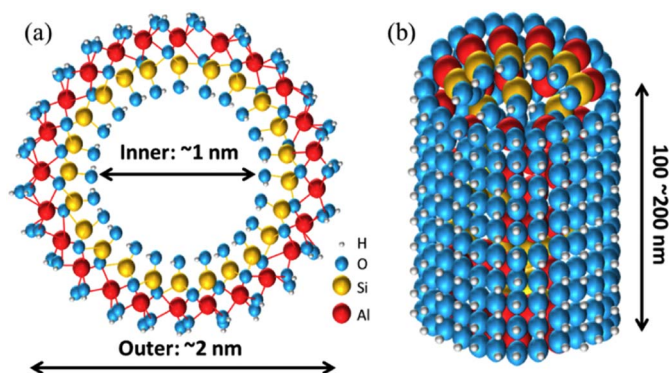


Fig. 1. Atomic structure of INTs viewed (a) along the axial direction and (b) from the side with three-dimensional view.

China. *N,N*-dimethylacetamide (DMAc, > 99%), tetraethyl orthosilicate (TEOS), sodium hydroxide (NaOH), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$), sodium hypochlorite (NaClO), sodium bisulphite (NaHSO_3) and sodium chloride (NaCl) were all commercial products from Sinopharm Chemical Reagent Co. Ltd. Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, AR, Aladdin), *m*-phenylenediamine (MPD, > 99%, Acros Organics), trimesoyl chloride (TMC, ~98%, Aladdin) and Isopar-G (Exxon Mobil Chemical Co.) were used as received.

2.2. Synthesis of imogolite nanotubes (INTs)

The synthesis of INTs was followed the method of Arancibia-Miranda et al. [29]. The aluminum and silicon sources of imogolite come from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and TEOS, respectively. The TEOS was added to an aqueous solution of 5 mM $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to obtain a mixed solution with a final Si/Al mole ratio of 0.5. The aforementioned mixed solution was stirred vigorously for 1 h at room temperature. Then a 1×10^{-2} M NaOH solution was added to the mixed solution until an Al:Si:OH mole ratio of 2:1:4 was obtained. The resulting clear solution was reacted at 95 °C for 5 days. The mixture was cooled down to room temperature and then adjusted to pH = 8 with 0.1 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ to yield a transparent gel. The gel was centrifuged at 9000 rpm for 15 min and then dried in a vacuum oven at 60 °C for 24 h. The dried imogolite was milled into powders.

2.3. Characterization of INTs

The structure of INTs was examined under a transmission electron microscope (TEM, JEOL2100, Japan) at 200 kV. Fourier transform infrared (FTIR) spectroscopy was performed using Nicolet 6700 to confirm the nanotube synthesis. The dried imogolite was mixed with KBr powder at the ratio of 1: 200 and then pressed into a flake. The spectra were obtained from 400 to 4000 cm^{-1} by cumulating 64 scans at a resolution of 2 cm^{-1} . X-ray diffraction (XRD, D8 Advance Davinci, Bruker) analysis was conducted with Cu: $K\alpha$ source ($\lambda = 1.54 \text{ \AA}$) over the 2θ range of 3–70°.

2.4. Preparation of PSf substrate

Table 1 presents the PSf dope solutions consisting of 15 wt% PSf, 85 wt% DMAc and different loading of INTs. An appropriate amount of INTs was first mixed in DMAc. Meanwhile, the mixture was stirred vigorously for 30 min at room temperature and sonicated for 30 min to ensure the homo-dispersion of nanotubes in the solvent. Then, PSf granules were added into the solution and stirred at 80 °C for 8 h until the solution became homogeneous. When the dope solution was cooled down, it was degassed for 5 min in vacuum. A casting knife setting at a gate height of 100 μm was used to cast the dope solution on a clean glass plate, which was then immediately immersed in the water coagulation bath containing 0.3% (v/v) DMAc to initiate a phase inversion. After membrane formation for 10 min, the membranes were transferred to another water bath and stored for at least 1 day to remove the residual solvent. In terms of concentration of the embedded INTs, the PSf substrates are labeled as Substrate (control), Substrate

Table 1
The composition of dope solutions for PSf substrates.

PSf substrates	Composition of dope solutions		
	PSf (wt%)	DMAc (wt%)	INTs (wt%)
Substrate (control)	15	85	0
Substrate 0.33	15	85	0.33
Substrate 0.66	15	85	0.66
Substrate 1.0	15	85	1.0

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