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Synthesis of novel graphene oxide-polyimide hollow fiber membranes for seawater desalination

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ABSTRACT

Hollow fiber membranes are more favorable for the fabrication of membrane modules in industry because of its high membrane area to module volume ratios. In the present work, we reported the preparation of novel graphene oxide (GO)/polyimide (PI) hollow fiber membranes for the first time by direct spinning of a GO/PI suspension via a coaxial two-capillary spinning strategy. The structure and morphology of GO/PI hollow fiber membrane was characterized by using XRD, FT-IR and FESEM. The GO nanosheets can homogeneously be dispersed in the PI matrix to form continuous and robust membranes due to a good compatibility between GO and PI, and GO/PI hollow fiber membrane shows a typical asymmetric structure. The performances of the GO/PI hollow fiber membrane were evaluated for desalination of seawater by pervaporation. The GO/PI hollow fiber membrane displays excellent water permeability and salt rejection for desalination of different concentrations of seawater. At 90 °C, a high water flux (15.6 kg m^{-2} h^{-1}) and a high salt rejection (99.8%) can be obtained. Further, the GO/PI hollow fiber membrane displays a high stability for seawater desalination with a long time measurement.

1. Introduction

The ever-rising demand to provide available and safe drinking water is an on-going global challenge due to the intense growth of population and aggravation of water pollution [1,2]. Among the different strategies to solve this problem, desalination is one of the most important and promising methods for production of freshwater [3,4]. However, large energy requirements and high capital costs are two critical factors which limit the development of desalination. Comparing to other desalination methods, membrane-assisted desalination technologies have obvious advantages, including lower energy consumption, low chemical sludge effluent, and excellent separation efficiency [5–8]. So far, although polymeric membranes are widely used in seawater desalination, they are usually unstable under a harsh separation condition [9,10]. Therefore, it is high desired to develop a novel membrane with high stability and high ions rejection for seawater desalination [11,12].

Recently, graphene-based membranes have attracted immense interest for water purification [13–15]. In particular, grapheme oxide (GO), an atomic-layer thick nanosheet containing oxygen-rich functional groups, has drawn much attention for the fabrication of molecular sieve membranes [16–24]. Through simple vacuum filtration or layer-by-layer (LBL) deposition of GO suspension, molecular or ionic sieving GO membranes can be easily prepared on various substrates. Further, as a derivative of graphene but containing oxygen-rich functional groups such as hydroxyl, epoxy groups, the GO membranes show preferential water adsorption ability and fast water diffusion through the GO membrane [25,26], thus leading to high water permeability. Considering that the actual diffusion path of GO (0.3 nm) [27] is just between the size of water molecules (0.26 nm) and hydrated ions (e.g. Na^+ 0.72 nm, K^+ 0.66 nm, Ca^{2+} 0.82 nm, Mg^{2+} 0.86 nm, Cl^- 0.66 nm), the GO membranes have shown high salt rejections in seawater desalination [28,29].

Since the mechanical strength of the GO membranes is not as good as organic polymer membranes due to electrostatic repulsion [30] or under mechanical stress [31], the GO membrane is easily destroyed in the practical applications. Therefore, the development of GO/polymer mixed matrix membranes (MMMs) is a helpful strategy to improve the mechanical property of GO membranes [32–34]. Recently, we have developed a GO/PI (polyimide) MMM for seawater desalination by dispersing GO into PI through the wet phase inversion method. It is found that the GO/PI MMM display excellent water permeability and salt rejection for seawater desalination. At 90 °C, the GO/PI MMMs

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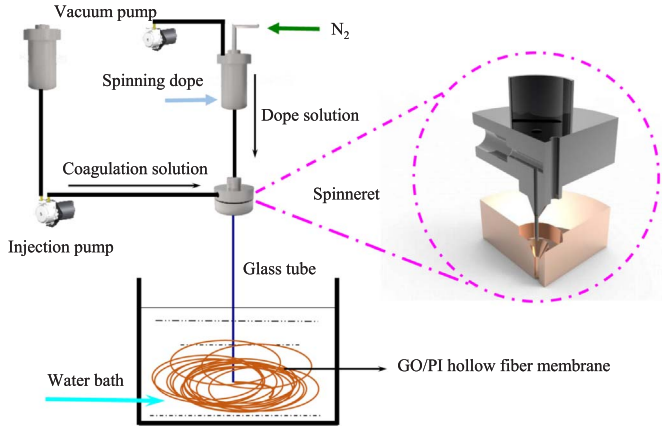

Fig. 1. Schematic diagram of the preparation of GO/PI hollow fiber membranes by direct spinning of a GO/PI suspension via phase inversion in water/NMP coagulation.

exhibit a high water flux (36.1 kg m^{-2} h^{-1}) and a high salt rejection (99.9%) for desalination of 3.5 wt% seawater [35]. However, it should be noted that most GO membranes are prepared on the flat or tubular supports, thus the packing density (i.e., membrane separation area/module volume ratio) of the separation module is relatively low. Hollow fiber membranes, often with a diameter of 1 mm or even less, are more favorable for the fabrication of membrane modules in industry because they can obtain high membrane area to module volume ratios (up to 9000 m^2/m^3). There are a few reports of GO membranes supported on ceramic hollow fiber to improve the permeance and selectivity [31,36]. To the best of our knowledge, however, there is no report of GO-based hollow fiber membrane for seawater desalination. In the present work, we develop a novel GO/PI hollow fiber membrane by direct spinning of a GO/PI suspension via a coaxial two-capillary spinning strategy (Fig. 1).

2. Experimental

2.1. Materials

All reagents were used as received without further purification: sodium nitrate ($NaNO_3$, AR, 99%), potassium permanganate ($KMnO_4$, AR, 99.5%), concentrated sulfuric acid (H_2SO_4, AR, 98%), ethanol (AR, 99.7%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Graphite powder (G; 2000 mesh), hydrogen peroxide (H_2O_2, AR, 30 wt%), N-methyl-2-pyrrolidinone (NMP, GC, 99.9%) and polyvinylpyrrolidone (PVP, K29-32) were supplied by Aladdin Co., Ltd. Polyimide (PI) resin powder was obtained from Alfa Aesar and was dried under vacuum before use (overnight at 100 °C).

2.2. Preparation of GO nanosheets and GO/PI hollow fibers

GO aqueous suspensions was prepared by the modified Hummers' method [37,38] using flake graphite powder as starting material according to the procedure as reported in the literature [28,29]. The resulting GO aqueous dispersion was sonicated for 30 min followed by centrifugation at 8000 rpm for 30 min to remove the unoxidized graphite. And then, the GO powder was obtained by freeze drying overnight.

The asymmetric GO/PI hollow fiber membranes were prepared by direct spinning of a GO/PI suspension via phase inversion in water/NMP coagulation (Fig. 1). In brief, 0.67 g GO were dispersed in 50 mL NMP by ultrasonication for 1 h. After 10 min of vigorous stirring, 9.5 g PI was added into the GO solution sequentially at 40 °C with vigorous stirring. Afterwards, 0.5 g PVP was added, followed by 2 h of stirring to form a homogenous dope solution. The dope solutions were loaded in the spinning system after being fully degassed by vacuum pump.

The detailed description of hollow fiber spinning can be found in elsewhere [39,40]. The spinning parameters were listed in Table 1, all other spinning parameters were kept constant: a single-layer spinneret with an outer diameter of 2.0 mm, inter diameter of 1.0 mm, and ambient temperature (25 °C) for spinning. N_2 pressure is applied to push the GO out of the spinneret and into the water bath solution, accompanied with a flow of the coagulation solution at a proper rate out from the core capillary that is controlled by the injection pump, and thus the GO/PI hollow fiber membranes are continuously produced. After primary phase separation and membrane formation, the GO/PI hollow fiber membranes were immersed into fresh distilled water for 24 h to ensure completion of phase separation and removal of excess solvents. The GO/PI hollow fiber membranes were dried at 60 °C for 1 h, and then stored for following characterizations and seawater desalination. For comparison, pristine PI hollow fiber membranes were also synthesized via similar procedure without addition of GO nanosheets.

2.3. Characterization of the GO/PI and PI hollow fiber membranes

Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 27) was used to characterize the surface properties of the GO, PI and GO/PI hollow fiber membranes. X-ray diffraction (XRD) was used to characterize the microstructures of GO, PI and GO/PI hollow fiber membranes. XRD analyses were recorded on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation at 40 kV and 40 mA. The X-ray photoelectron spectroscopy (XPS) was employed to characterize the elementary compositions of the GO sheets. Field emission scanning electron microscopy (FESEM, Hitach, S-4800) was used to examine the morphology of the GO/PI and PI hollow fiber membranes. The mechanical properties of the hollow fiber membranes were evaluated by measuring tensile strength and Young's modulus with an Instron 5567 machine at a constant speed of 3 mm/min. The N2 adsorption-desorption isotherms of the GO/PI and PI hollow fiber were measured in the pressure range up to 1 atm at 77 K. Before measurements, every sample was degassed at 383 K for 6 h under vacuum.

2.4. Seawater desalination through the GO/PI hollow fiber membranes by pervaporation

The desalination performances of the GO/PI hollow fiber membranes for different temperature of seawater were measured by pervaporation [28,29,41]. The GO/PI hollow fiber membranes with an

Table 1
Spinning conditions for preparation of PI and GO/PI hollow fiber membranes.

Membrane	Spinning parameters				
	Dope composition (wt%)	Bore fluid composition (wt%)	Bore flow rate (mL min^{-1})	Membrane OD (μm)	Wall thickness (μm)
PI	14.6/2.0/9.1/74.3 (PI/PVP/EtOH/NMP)	30/70 (NMP/water)	5	2000	1000
GO/PI	1.0/14.4/2.0/73.6 (GO/PI/PVP/EtOH/NMP)	30/70 (NMP/water)	5	2000	1000