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Covalent synthesis of three-dimensional graphene oxide framework (GOF) membrane for seawater desalination

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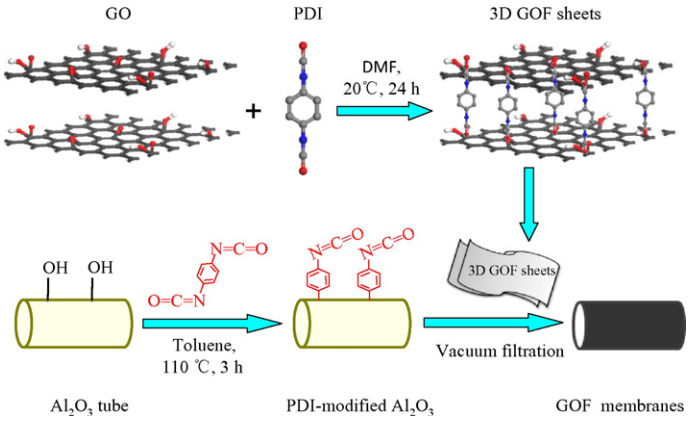
HIGHLIGHTS

- Covalent modification strategy is developed to prepare graphene oxide framework.
- Tubular GOF membrane was prepared through vacuum filtration of GOF suspensions.
- GOF membranes on PDI-modified α-Al_2O_3 tube display high desalination performances.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, we reported the preparation of graphene oxide framework (GOF) membrane through vacuum filtration of GOF suspension for seawater desalination. Firstly, 1, 4-phenylene diisocyanate (PDI) was selected as cross-linking for covalent modification of GO nanosheets to prepare three-dimensional GOF. Secondly, micron-thickness GOF membrane was prepared on the PDI-modified α-Al_2O_3 tube through vacuum filtration of GOF suspension. The developed GOF membrane was evaluated for seawater desalination by pervaporation. Attributing to a three-dimensional structure, the resistance of the mass transferring through GOF membrane can be reduced, thus the water flux of the GOF membranes can be increased significantly. For an 18 μm thickness of GOF membrane at 90 °C, the water flux is 11.4 $kg \cdot m^{-2} \cdot h^{-1}$ and ion rejection is over 99.9% for desalination of 3.5 wt.% seawater. Further, the GOF membrane also displays high stability for seawater desalination. This high separation performance combined with high stability and facile fabrication road of the GOF membrane suggests that the developed GOF membrane is a promising candidate for desalination of seawater and brackish water.

1. Introduction

Due to the increase of water demand and aggravation of water pollution, the shortage of freshwater resource has already become a worldwide problem. Recently, considerable efforts have been afforded to obtain drinking water from saltwater, including seawater and brackish

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water desalination [1]. However, large energy requirements and high capital costs are two critical factors that limit the developing of desalination. Compared to other desalination methods, reverse osmosis (RO) have been widely used in commercial applications [2]. However, a high pressure is normally required during the RO separation process [3]. Pervaporation has been widely applied for the separation of organics/water mixtures due to its low energy consumption and ease of operation. Recently, pervaporation is also recommended to be a promising technique for seawater desalination [4–6].

Currently, significant efforts have been paid to develop new membranes such as polymeric membranes and zeolite membranes for seawater desalination by pervaporation. Although polymeric membranes are popular in reverse osmosis desalination [7], inherently low stability of the polymeric membranes limits their application for pervaporation [8,9]. Zeolite membranes, with well-defined pore/channel structure and high stability [10], have attracted considerable attention for desalination. Unfortunately, poor compatibility between the zeolite layer and the support usually results in the formation of defects during membrane preparation. Therefore, it is highly desired to develop novel membrane materials with high stability and high ions rejection for seawater desalination.

Recently, the studies on the use of graphene-based membranes for water purification by pervaporation have attracted much interest to meet the desire of new membrane materials [11–13]. In particular, graphene oxide (GO), a new intriguing material with an ultra-thin two-dimensional structure and abundant oxygen-containing groups, has displayed outstanding water permeability [14–16]. The fabrication of GO membranes by vacuum filtration or layer-by-layer (LBL) deposition of GO suspension has been widely studied for the separation of gases or liquids [17–20]. Attributing to the preferential water adsorption ability and fast water diffusivity through the GO membrane, the GO membranes show excellent performance in water permeation [21]. Further, since the actual diffusion path of GO (0.3 nm) [22] 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), all hydrated ions can be effectively excluded by GO membranes. Therefore, it can be expected that GO membranes can show high salt rejections for seawater desalination.

However, because the mechanical strength of the inorganic GO membranes is not as good as organic polymer membranes, the thin GO membrane is easy to be destroyed in the practical applications. The preparation of thick GO membranes is a simple way to enhance the mechanical stability. However, there is an opposite relationship between the water flux and the thickness of GO membrane [23–25]. Indeed, as reported previously [14], even for a sub-micrometer thick GO membrane, it was completely impermeable to liquids, vapors and gases since the GO membrane is too tightly packed to let the molecules go through. Therefore, it is challenged to develop a high permeable GO membrane. So far, guided by the intrinsic properties of GO nanosheets, a few attempts have been carried out to design the microstructure of GO membranes, usually making a compromise between mechanical stability and separation performances [26,27]. Therefore, three dimensional graphene oxide-framework (GOF) membranes are desired to be fabricated to improve the membranes mechanical stability and separation performances simultaneously.

As reported previously [28,29], organic isocyanates can react easily with the hydroxyl and carboxyl groups of graphene oxide to form carbamate and amide functionalities. Consequently, strong covalent bonds can be formed between the neighboring GO nanosheets through the linking of isocyanates, leading to formation of three-dimensional GOF materials. In this study, 1, 4-phenylene diisocyanate (PDI) is selected as a cross-linking for covalent modification of GO nanosheets to prepare three-dimensional GOF, and then GOF membranes are prepared on the PDI-modified α-Al_2O_3 tubes through vacuum filtration of GOF suspension, as shown in Fig. 1.

2. Experimental

2.1. Materials

All reagents were used as received without further purification: concentrated sulfuric acid (H_2SO_4, AR, 98%), sodium nitrate ($NaNO_3$, AR, 99%) and potassium permanganate ($KMnO_4$, AR, 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hydrogen peroxide (H_2O_2, AR, 30 wt.%), *N*, *N*-dimethylformamide (DMF, GC, 99.9%), Graphite powder (G; 2000 mesh) and 1, 4-phenylene diisocyanate (PDI, 98%) were supplied by Aladdin Co., Ltd. Porous α-Al_2O_3 tubes (Jiexi Lishun Technology Co., Guangdong, China: 12 mm outside diameter, 9 mm inside diameter, 75 mm length, ca. 1.0 μm pore size, 30% porosity) were used as supports.

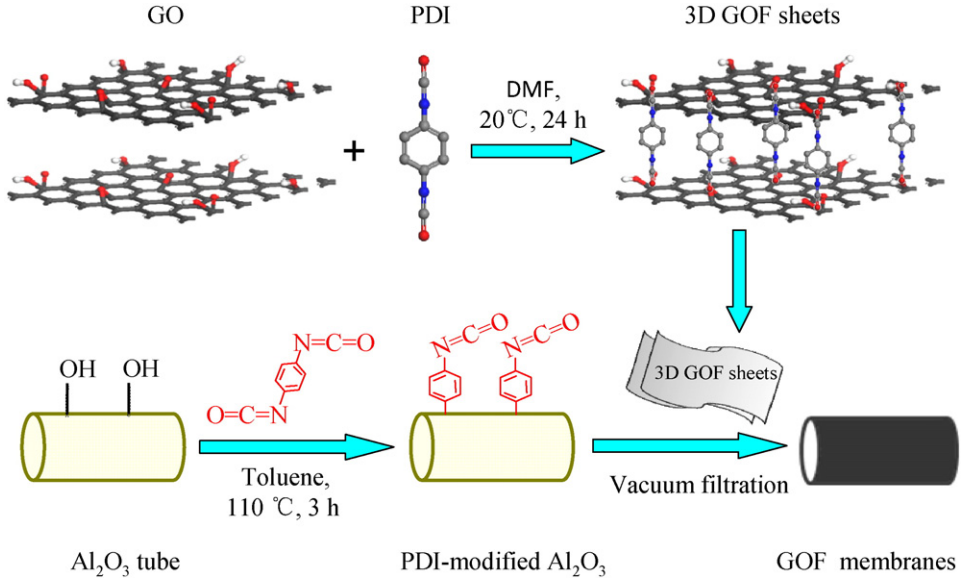

Fig. 1. Scheme of the synthesis of GOF membranes on the PDI-modified α-Al_2O_3 tubes through vacuum filtration method.