



Enhanced desalination performance of forward osmosis membranes based on reduced graphene oxide laminates coated with hydrophilic polydopamine



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ABSTRACT

Forward osmosis (FO) processes have been recognized as a low energy required next-generation desalination technology, but the low performance of polymeric membranes remains a bottleneck in the practical application of FO. Graphene oxide (GO) membranes possess a huge potential as an alternative to polymeric membranes because of their facile fabrication procedure, ultra-thin thickness, controllable pore size, and outperformance of competing materials in terms of water transport rate; the low stability of GO laminates under water and their hydrophobic property (if GO laminates are reduced) remain as problems requiring solution prior to their practical implementation. To solve these problems, herein, the chemical reduction of GO laminates and a hydrophilic adhesive polydopamine (pDA) layer were applied. Reduced GO (rGO) laminates sustainably retained their compacted nanochannels (3.45 Å) compared to pristine GO laminates, which increased the selectivity of hydrated ions. In addition, adding a pDA coating onto the rGO laminates improved the hydrophilicity of the rGO laminate surface, which accelerated the water absorption speed. As a result of these synergistic effects, pDA-coated rGO (pDA-rGO) membranes achieved an outstanding water flux of 36.6 L/m²·h, with a reverse solute flux of 0.042 mol/m²·h and a high salt rejection rate of 92.0% in FO.

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1. Introduction

Forward osmosis (FO) is driven by the osmotic pressure that is naturally generated by the concentration gradient across a semi-permeable membrane for water desalination; FO produces water at a lower energy consumption than reverse osmosis (RO), which uses hydraulic pressure as the driving force. Consequently, FO has emerged as a future desalination technology, and has been in rapid development over the last decade. However, several challenges with FO remain (e.g., membrane fouling, low water flux, and reverse solute flux) prior to its practical application in the field of desalination [1]. These challenges are mainly related to the fact that only a few types of polymeric FO membranes are commercially available. Moreover, state-of-the-art polymeric FO membranes do

not offer sufficient water permeability and salt rejection. Therefore, alternative membranes for current polymeric FO membranes need to be developed to further improve the performance of FO processes.

Recently, the potential of nanoporous graphene membranes, having high mechanical strength, atomic thickness, and fine-tuned pores, has been identified for use in a next-generation membrane that has ultrafast water flux and almost flawless salt rejection [2–5]. Using molecular dynamics (MD) simulation, Cohen-Tanugi et al. [2] predicted that single-layer graphene membranes having functionalized nanopores would have hundreds of times higher water permeability, with almost 100% salt rejection, than commercial polymeric RO membranes. Gai et al. [4] exhibited functionalized porous graphene membranes displaying amazing water flux and salt rejection during FO processes. Furthermore, actual porous graphene membrane fabrications have been attempted by forming nanopores in a single-layer graphene sheet using various methods (e.g., combination of ion bombardment and chemical

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etching [6], focused ion beam irradiation [7], and oxygen plasma etching [8]). In particular, a nanoporous graphene membrane perforated by oxygen plasma etching showed an excellent water flux of $10^6 \text{ g/m}^2 \cdot \text{s}$ with almost 100% salt rejection [8]. However, synthesis of scalable defect-free single-layer and formation of high-density well-defined nanopores in graphene sheets remain significantly challenging. Moreover, the high price of scalable defect-free single-layer graphene also inhibits the commercialization of porous graphene membranes [9].

As an alternative for nanoporous graphene membranes, graphene oxide (GO) membranes have attracted the attention of researchers [9–11]. GO is a single-layer graphene based nanomaterial having plentiful oxygen functional groups in the form of epoxy, hydroxyl, carboxyl, and others [12]. As a novel membrane material, GO has excellent characteristics (e.g., inexpensive mass-production cost, high chemical stability, high hydrophilicity, negatively charged surface and strong anti-bacterial propensity) [10,13,14]. By stacking GO nanosheets, GO membranes can be easily fabricated via several facile methods, such as vacuum-assisted filtration and drop casting [10,15,16]. Nanochannels formed between stacked GO nanosheets offer a low-friction pathway for the ultra-fast transport of water molecules. Due to non-oxidized areas on the surface of GO membranes, water molecules could also be transported at ultrafast speeds with low friction [17,18]. In addition, the GO nanochannels naturally made in a laminated structure provide precise selectivity for ionic and molecular species, based on size exclusion [10,18–20].

However, serious drawbacks prior to the real application of GO membranes remain. In particular, GO laminates are highly susceptible to redispersal into water, and the size of GO nanochannels becomes enlarged due to the high hydrophilicity of GO nanosheets. These phenomena negatively affect the stability and selectivity of GO membranes [20].

Herein, to overcome these challenges and finally use GO membranes in FO desalination processes, two technical strategies are adopted. Initially, GO laminates are chemically reduced in order to remove hydrophilic functional groups from GO. Consequently, the stability of GO laminates can be improved, and the nanochannels can be narrowed, which increases the rejection of ionic species for desalination [15], though the tightened rGO nanochannels and the hydrophobic surface of rGO laminates would be obstructive factors against water transport. However, water permeability across rGO laminates can be enhanced by reducing the thickness of rGO laminates within a nanometer scale. Han et al. [21] reported that the water permeability of rGO membranes increased with decreases in the thickness of rGO laminates. In their study, the thinnest rGO laminates achieved the highest water permeability of $21.81 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$. In addition, it was reported that the ultrafast water flow in the core of carbon nanotubes (CNTs) is due to the hydrophobic inner wall of the CNTs, though the high hydrophobic inlet of CNTs cannot allow water to readily enter the core of CNTs [22]. To reduce the entrance resistance, previous studies have introduced hydrophilic functional groups [23,24]. The water transport in the interior of CNTs is similar to that in GO nanochannels [10]; if the surface of rGO laminates is more hydrophilic, water could more readily flow into the nanochannels formed in rGO laminates. Therefore, a hydrophilic polydopamine (pDA) thin layer was finally deposited onto the rGO laminates to increase the efficiency of the water uptake into rGO nanochannels.

pDA is an adhesive mussel-foot-protein-inspired polymeric substance that can be easily and strongly deposited on any substrate and thereby increase the hydrophilicity, as pDA contains catechol and amine functional groups [25]. In this study, pDA-coated rGO (pDA-rGO) membranes exhibit superior FO desalination performance, with improved water flux and lowered reverse solute permeation compared to either a commercial cellulose

triacetate embedded support-type (CTA-ES) membrane or a pristine rGO membrane, indicating that pDA-rGO membranes have great potential as a novel membrane for high-performance FO desalination processes.

2. Experimental

2.1. Synthesis of pDA-rGO membrane

The fabrication procedure of the pDA-rGO membrane is described in Fig. 1. First, an ultra-high concentration single-layer GO aqueous solution (6.2 mg/mL) was purchased from Graphene Supermarket (Calverton, US), and was diluted with deionized (DI) water to prepare a GO aqueous solution of 0.006 mg/mL. The prepared GO aqueous solution (0.006 mg/mL) was then sonicated for 30 min, and then filtered through a mixed cellulose ester membrane having a $0.2 \mu\text{m}$ pore (MCE; 47 mm area, Advantec MFS, Inc., Japan) using a vacuum-assisted filtration system. The GO laminates on the MCE membranes were dried at 40°C for more than 24 h. To reduce the resultant GO laminates on the MCE membrane, the GO laminates were exposed to hydriodic acid vapor (HI; Sigma Aldrich, USA) [15]. The rGO membrane was left at room temperature for 1 day. Next, the rGO membrane was fully dipped in a 2.0 g/L dopamine solution (pH 8.5) for 1 h. The 2.0 g/L dopamine solution was prepared by adding dopamine hydrochloride (Sigma Aldrich Co. LLC., USA) to a Tris-HCl buffer (15 mM, pH 8.5). The resulting pDA-rGO membrane was dried at 40°C and stored in a desiccator prior to use.

2.2. Membrane characterization

The characteristics (e.g., surface morphology, thickness, hydrophilicity, chemical structure, and nanochannel size) of the prepared GO, rGO and pDA-rGO membranes were investigated. The membrane morphology and thickness were observed using scanning electron microscopy (SEM; S-4700, Hitachi, Japan) and a stylus profiler system (Dektak XT, Bruker Cooperation, US), respectively. The membrane hydrophilicity was determined by measuring the contact angle using a goniometer (Phoenix 300, Surface Electro Optics Co., South Korea). The chemical structure of the membranes was analyzed using X-ray photoelectron spectroscopy (XPS; VG Microtech MultiLab ESCA 2000, Thermo VG Scientific, United Kingdom) and Fourier transform infrared spectroscopy (FT-IR; Frontier FT-IR/NIR, Perkin Elmer, USA). The nanochannels formed between GO (or rGO) nanosheets in the membranes were characterized using X-ray diffraction (XRD; X'pert PRO, PANalytical, Netherlands).

2.3. Ion transport and salt rejection

A two-compartment diffusion cell was prepared to observe the ion transport across a membrane (Fig. 2(a)). A test membrane (effective area: 0.73 cm^2) was installed between two compartments. For the real-time monitoring of ion permeability, the probe of a total dissolved solids (TDS) meter was inserted into one compartment. The compartment having the TDS probe (COND610, Eutech Instruments, Singapore) was filled with 100 mL of DI water, and the other compartment was filled with 100 mL of 0.6 M NaCl solution.

2.4. Membrane performance evaluation in an FO system

To evaluate the membrane performance in FO, a lab-scale FO system was set up (Fig. 2(b)). The system has a two-compartment membrane cell, separated equally using a test membrane

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