



Chemically crosslinked rGO laminate film as an ion selective barrier of composite membrane



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ABSTRACT

In this research, a novel approach of sulfonation followed by mild reduction was employed first time to prepare well separated rGO laminate composite membranes. The combined multistep approach offers hydrophilic regions as well as suitable interlayer spacing of 0.63 nm and 0.74 nm for ion selectivity and water permeation. In-situ Crosslinking reaction has been conducted on the assembled rGO film to successfully improve the stability of the rGO film in water. The promising water permeability of 61.7 LMH/kPa was achieved from optimized rGO interlayer distance by carefully controlled sulfonation and partial reduction conditions (sample Low-R). It was found that the net surface charges Donnan exclusion mechanism played a significant role in the salt rejection efficiency, which was subject to the ratio of cationic and anionic species valency present in the solution. The prepared rGO membrane High-R achieved 80.5% rejection of Na₂SO₄, followed by 52.0% rejection of NaCl, and 13.7% rejection of MgCl₂. It can be seen that there was an interplay between water flux and salt rejection performance, the balance can be achieved by adjusting the reduction conditions. Stronger reduction condition resulted in higher salt rejection rate, while the water flux would decrease to some extent, it was due to the less remaining surface functional groups and resulted in smaller interlayer distance. This research has tested and confirmed of using a novel approach, a relatively small quantity of well prepared and assembled two-dimensional rGO laminates could form an integrated barrier for effective ion selectivity.

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1. Introduction

Recently, the worsening global scarcity of freshwater resources [1,2] has driven the research attention to the non-conventional sources, such as oceans, groundwater and treated wastewater. Membrane processes such as ultrafiltration (UF), nanofiltration (NF), forward osmosis (FO) and reverse osmosis (RO) are the most effective strategies for fresh water augmentation [3,4]. Among these processes, RO membrane desalination process is presently considered as the state of the art desalination process, and its energy-efficiency has been greatly improved in the past decades [5,6]. However, traditional membrane processes still need further improvement to overcome important technical limitations on water flux, salt rejection and fouling resistance [7].

Among many types of nanostructured materials, the two-dimensional (2D) graphene materials [8,9] and graphene oxide (GO) [10] are considered to be promising for the fabrication of

desalination membranes [11,12], due to their nearly frictionless 2D surface prompting the fast flow of water molecules and good selectivity for ions [13,14]. Free-standing graphene sheet created with nanopores can play a valuable role to study the sieving mechanism in separation of salt ions and water [15,16], but it is difficult to scale up the production of large size graphene sheets with precisely controlled pore size and high pore density for desalination application. In a different approach, GO, with abundant functional groups, i.e. epoxide and hydroxyl on the basal planes, and carboxyl on the edges, possesses good workability and flexibility of surface functionalization for desalination membrane fabrication [17–19].

GO sheets can be assembled on the surface of membranes with interlocked structure and controlled thickness by processes such as, drop-casting [20], spin-coating [21], layer by layer assembly [22], dip-coating [23,24], and vacuum filtration [25].

Demonstrated by experiments, it was found that during the desalination process water molecules could permeate through the interconnected nanochannels formed between GO nanosheets [14,26]. Previous research in our group have reported that

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interlayer distance between the graphene nanosheets can be affected and adjusted by a multistep sulfonation and partial reduction process [27–29]. By forming covalent bond between the oxygen containing functional groups on the GO nanosheets, the stability of the GO in the water can be improved [30]. The hydrophobic non-oxidized region on the surface was the primary pathways for transport of water molecules [31], whereas the hydrophilic oxidized region of GO sheets could act as supporting points to avoid the diminishing of the interlayer space from aggregation, as well as the active sites for covalently crosslinking to overcome the hydration force of GO nanosheets, so as to improve the stability of the GO layers [22,32].

Recently, many novel development of GO based desalination membranes were reported. Mi et al. fabricated GO based membranes using layer-by-layer assembly of negatively charged GO nanosheets on Polyacrylonitrile (PAH) and polydopamine-coated polysulfone support by using different approach [22,37]. Wang et al. [32] have synthesized a series of covalently crosslinked GO membranes by esterification reactions. The graphene assisted membranes prepared by these research have demonstrated different levels of separation functions. Some have demonstrated successful separation of organic molecules such as sucrose and dyes from water. However, up until now, use graphene-assisted membrane to reject divalent ions and monovalent ions such as Mg^{2+} and Na^+ still remains at relatively low efficiency. The ion selectivity mechanism of the membrane barrier built from these graphene sheet layers has not been fully investigated and are still less clearly understood.

This study is dedicate to the synthesis and assembly of the reduced graphene oxide (rGO) sheets into multiple-layered laminate film on membrane substrate. Novel sulfonation and partial reduction approaches were employed to adjust interlayer distance (in sub-nanometer range), and achieve narrow-size distribution of the nano-channels formed between the graphene sheets (Fig. 1 (a)). The stability of GO membrane in water was effectively addressed by cross-linking of the oxygen containing functional groups on the rGO nanosheets (Fig. 1(b)). Major challenges faced

by graphene membranes such as lack of stability in water and low ion selectivity have been successfully addressed.

2. Materials and methods

2.1. Materials

Graphite flakes were purchased from Bay Carbon Ltd. (USA). All the chemical agents used in this experiment were supplied by Sigma-Aldrich Ltd., including sulfuric acid (98 wt%), nitric acid (65 wt%), Hydrochloride acid (37 wt%), ammonia solution (35 wt%), hydrogen peroxide (30 wt%), hydrazine monohydrate (65 wt%), potassium permanganate, sulfanilic acid, sodium nitrite, sodium nitrate, sodium chloride, magnesium sulfate, manganese sulfate, magnesium chloride and potassium chloride.

2.2. Synthesis, sulfonation and partial reduction of GO nanosheets

The GO nanosheets used for membrane fabrication were prepared through a modified Hummers method, followed by sulfonation reaction, the detailed procedure was reported in our previous articles [33–37]. In this experiment, GO nanosheets were prepared and then used as well dispersed solution. The highly soluble GO solution was obtained by the exfoliation of graphite oxide through sonication treatment for 1 h by using a tip ultrasonic instrument at an amplitude of 40%. In order to achieve good solubility of GO nanosheets in aqueous solution, further functionalization steps were carried out after the oxidation procedure.

The exfoliated GO was functionalized by grafting negatively charged sulfonic groups using aryl diazonium salt by using a typical sulfonation procedure reported in our previous research [27]. Lastly, the sulfonated GO suspension was undergone a mild reduction process by using two different quantities of hydrazine monohydrate, and the partially reduced sulfonated rGO solution was obtained. The pH of sulfonated GO suspension was adjusted to ca. 9–10 by ammonia solution before reduction. For 1000 ml

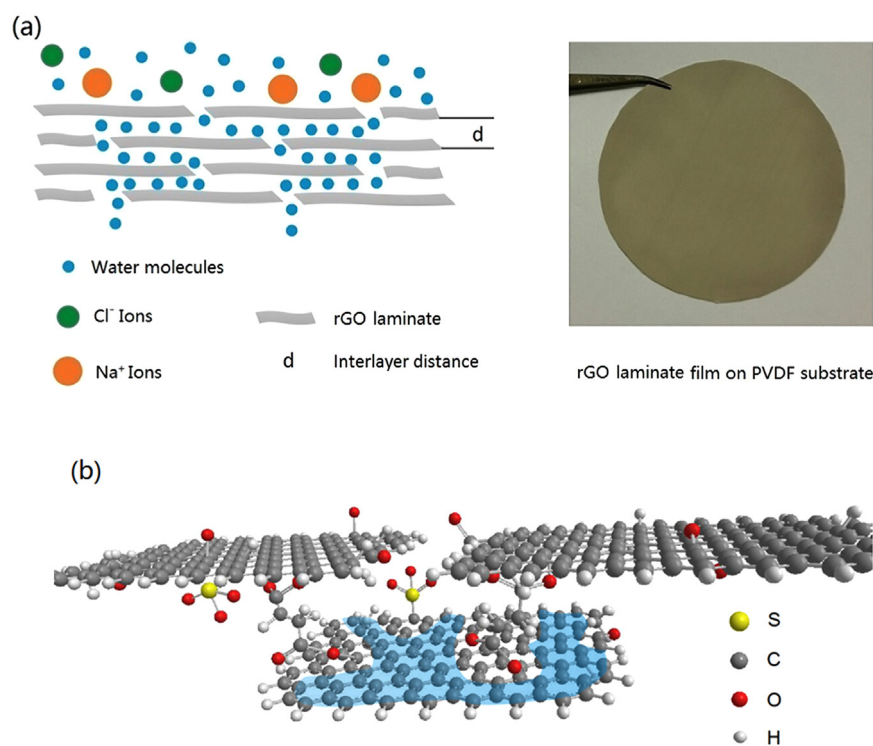


Fig. 1. Schematic diagram of (a) the rGO membrane for desalination and (b) crosslinking mechanism of rGO laminates.

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