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## Enhanced water permeation through sodium alginate membranes by incorporating graphene oxides

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## ABSTRACT

Pristine graphene oxide (pGO) and reduced graphene oxide (rGO) nanosheets with different physical and chemical structures were prepared, and blended into sodium alginate matrix to fabricate two types of hybrid membranes. Compared with pGO, rGO possessed smaller nanosheet size, more structural defects, less negative charges, less oxygen-containing groups, and more non-oxide regions. The hybrid membranes exhibited brick-and-mortar morphology, unusual crystallinity change, and increased free volume. Swelling resistance and mechanical stability of the hybrid membranes were both enhanced. Pervaporation dehydration was conducted utilizing ethanol/water mixture as model to explore the selective water permeation through hybrid membranes. Due to synergy between permselectivity of water channels and crystallinity of polymer matrix, the hybrid membranes, particularly for rGO-filled membranes, exhibited improved separation performance with increased separation factor and an unusual change of permeation flux. When the rGO content was 1.6 wt%, optimum separation performance with a separation factor of 1566 and a permeation flux of 1699 g/(m<sup>2</sup>h) was achieved. The transport mechanism was investigated based on transport property comparison of the two types of membranes, revealing that more water channels with higher selectivity could be constructed and controlled by graphene oxide structure. Moreover, the hybrid membrane displayed a good long-term operation stability.

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## 1. Introduction

Graphene, as a monolayer of sp<sup>2</sup> carbon atoms, has received tremendous attention due to its large theoretical specific surface area, high electrical conductivity, and superior mechanical strength [1]. Graphene oxide (GO) with oxygen-containing groups attached on its edge and basal plane is a highly dispersible derivative of graphene [2]. Although impermeable to all molecules in defect-free form [3], the graphene membranes with well-designed nanopores or defects displayed extraordinary separation performances for different gases or liquids predicted by molecular dynamics simulations [4,5]. Nair et al. [6] fabricated submicrometer-thick GO membrane experimentally, which allowed unimpeded water permeation while blocking other liquids, vapors, and gases. This phenomenon was attributed to the low-friction rapid flow of water on the non-oxidized regions of GO

and the nanochannel networks formed by spaced GO nanosheets. Subsequently, several kinds of ultrathin GO membranes have been prepared and showed tremendous application potentials in gas separation [7,8], water purification [9], and pervaporation [10,11]. Their explorations on selective penetration mechanism revealed that molecular transport channels in GO membranes were constructed by the interlayer spacing, interlocking degree, and selective structural defects of GO nanosheets. The transport channels were strongly dependent on the GO structure, including physical structure (e.g., nanosheet size, charge density, structural defect degree, etc.) and chemical structure (e.g., oxygen-containing group content, non-oxidation domain, etc.). However, the GO membranes were fragile and thermolabile restricting their practical applications especially in liquid separation processes.

Since polymer–inorganic hybrid membrane can combine the excellent film forming ability of polymer and the unique property of inorganic constituent [12], polymer–GO membranes have drawn much interest in diverse separation processes. Through incorporating GO into different polymer matrices, the hybrid membranes showed higher water fluxes and better antifouling

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properties for nanofiltration or ultrafiltration [13,14]. The ionic conductivity of ion exchange membrane was enhanced by the incorporation of GO [15]. After reduction or sulfonation treatment of GO, the ionic conductivity of hybrid membranes was further improved with simultaneous suppression of alcohol transport [16,17]. As demonstrated by above works, GO showed great potential for the fabrication of hybrid separation membranes, and the modification of GO chemical structure could enhance the separation performance.

Owing to the anomalous water transport behavior between GO nanosheets [6,18], GO was speculated to be a useful filler of hybrid membrane for dehydration of organic/water mixture. Wang et al. [19] prepared hybrid membranes by incorporating GO into polyelectrolyte complexes through layer-by-layer self-assembly. The membranes exhibited enhanced selectivity for pervaporation dehydration of different solvent/water mixtures while the permeate flux declined. Suhas et al. [20] fabricated hybrid membranes incorporated with multi-layer graphene sheets, and the simultaneous increase of water permeance and selectivity was observed for isopropanol dehydration. Though encouraging results have been achieved, it needs to be pointed out that the existing works mainly investigated hybrid membranes incorporated with single type of GO (poly(ethyleneimine)-modified GO or highly oxygenated surface functionalized graphene). Furthermore, the change trend of water permeation flux in the presence of GO remains elusive. Recently, some researchers found that GO or functional graphene nanosheets had multiple effects on the crystallization of polymer chains [21–26], and even led to non-monotonic change of the polymer crystallinity in the hybrid membranes [27]. Consequently, more systematic exploitations are needed to correlate GO structure with the transport property and separation performance of hybrid membrane.

In this study, two types of GOs, pristine graphene oxide (pGO) and reduced graphene oxide (rGO) were prepared. The physical and chemical structures of GOs were characterized. Then different amounts of pGO and rGO were respectively incorporated into sodium alginate (SA) matrix to fabricate different types of hybrid membranes. Field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), positron annihilation lifetime spectroscopy (PALS), thermogravimetric analysis (TGA), and tensile test were utilized to characterize the morphology, crystallinity, free volume property, thermal stability, and mechanical stability of the membranes. Separation performances of the hybrid membranes were evaluated by pervaporation dehydration tests utilizing ethanol/water mixture as model. Furthermore, the correlations between GO structure and the selective water permeation through the hybrid membranes were investigated. The transport mechanism of the hybrid membranes was discussed as well.

## 2. Experimental

### 2.1. Materials

Natural graphite flake (2500 mesh) was purchased from Qingdao Tianhe Graphite Co. Ltd. (Shandong, China). Sodium alginate (SA) was supplied by Qingdao Bright Moon seaweed Group Co. Ltd. (Shandong, China). Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98 wt%), hydrochloric acid (HCl) and potassium permanganate ( $\text{KMnO}_4$ ) were gained from Tianjin Kewei Ltd. (Tianjin, China). Hydrogen peroxide aqueous solution ( $\text{H}_2\text{O}_2$ , 30 wt%), calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ), absolute ethanol and sodium nitrate ( $\text{NaNO}_3$ ) were bought from Tianjin Guangfu Technology Development Co. Ltd. (Tianjin, China). Polyacrylonitrile (PAN) ultrafiltration membranes used as membrane substrates with a molecular weight cut-off of 100 kDa were obtained from Shanghai MegaVision Membrane Engineering & Technology Co. Ltd. (Shanghai, China).

All the reagents were of analytical grade and used without further purification. Deionized water through a Millipore system (Milli-Q<sup>®</sup>) was used in all experiments.

### 2.2. Preparation of pGO

Pristine graphene oxide was prepared by modified Hummers method [28]. In a typical reaction, 5 g of graphite powder and 2.5 g of  $\text{NaNO}_3$  were added to 115 mL of 98 wt%  $\text{H}_2\text{SO}_4$  in an ice bath. Then 15 g of  $\text{KMnO}_4$  was added in batches to keep the temperature under 5 °C. After stirring for 2 h, the mixture was transferred into oil bath at  $35 \pm 2$  °C and stirred for 30 min. A 230 mL portion of water was added into the mixture gradually to keep the temperature below 100 °C. Afterwards the temperature was raised to 98 °C and kept for 3 h in order to improve the oxidation degree of graphite oxide. Followed by adding 20 mL of  $\text{H}_2\text{O}_2$ , the resulting viscous mud was diluted. Then the mixture was centrifuged and washed with water several times, and the concentrate was diluted and sonicated for 1 h. Finally, the yellow–brown pGO aqueous dispersion was obtained by centrifuging at 10,000 rpm to remove the large and not fully exfoliated parts.

### 2.3. Preparation of rGO

Reduced graphene oxide was prepared via a hydrothermal route which is simple, green and well controlled [29]. Since the reduction degree of pGO can be tuned by engineering the temperature and time, experimental parameters were determined to balance the dispersibility and reduction degree. In brief, a 70 mL portion of 0.5 mg/mL pGO aqueous suspension was transferred to a Teflonlined autoclave and heated at 150 °C for 2.5 h in a furnace. After cooled to room temperature, the resultant black rGO suspension was highly stable and homogeneous. There was no visible precipitate and agglomeration found even centrifuging at 10,000 rpm.

### 2.4. Fabrication of membranes

In a typical procedure, different amounts of pGO or rGO aqueous dispersion were diluted to 25 ml by water. 0.51 g of SA was dissolved in above solutions respectively under stirring at 30 °C for 5 h. After filtration and degassing, the homogenous mixture was spin-coated onto PAN substrates. The composite membranes were placed at room temperature for 24 h to evaporate the solvent. After immersed in 0.5 M  $\text{CaCl}_2$  solution for 10 min and rinsed with abundant water, the cross-linked membranes were obtained. For simplicity, the membrane samples were designated as SA–pGO-X/PAN or SA–rGO-X/PAN, where X represented the content of pGO or rGO in SA (wt%). The X varied from 0.4 to 2.4 for SA–pGO-X/PAN and from 0.4 to 2.0 for SA–rGO-X/PAN. For characterization and swelling study, the corresponding homogeneous membranes were fabricated on glass plates instead of PAN substrates following a similar preparation procedure and denoted as SA–pGO-X or SA–rGO-X.

### 2.5. Characterization of GOs and membranes

The morphology of GOs was observed by transmission electron microscopy (TEM, JEOL JEM-100CXII). Raman spectra of GOs were obtained by a DXR Smart Raman Spectrometer (Thermo Fisher Scientific). The surface charge properties of GOs were measured in their aqueous dispersions by a Brookhaven zeta-potential analyzer. The chemical properties of the GOs were characterized by Fourier transform infrared spectra (FT-IR, BRUKER Vertex 70). Wide-angle XRD patterns were used to investigate the crystallization properties of GOs and membranes by a D/MAX-2500 X-ray diffractometer ( $\text{CuK}\alpha$ ). The chemical compositions of GOs were characterized by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 1600

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