

Cation-dependent structural instability of graphene oxide membranes and its effect on membrane separation performance



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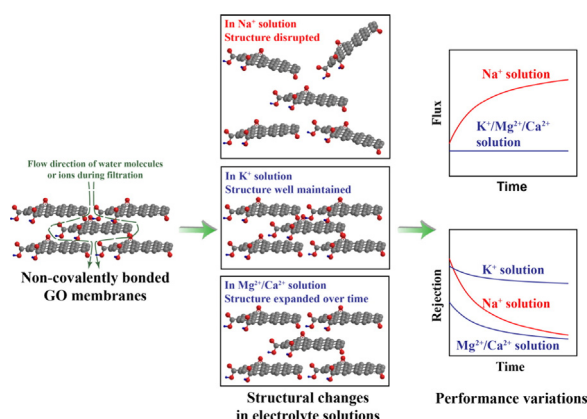
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HIGHLIGHTS

- The GO membrane structure was disrupted by Na⁺.
- The GO membrane structure was slightly expanded by Mg²⁺/Ca²⁺ and maintained by K⁺.
- The disruption effect of Na⁺ led to significantly increased flux of GO membranes.
- Degrees of salt rejection declines accorded with membrane structural instability.
- Na⁺ disrupted the membrane due to its large size but weak attractions with GO.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene oxide (GO) membranes formed by stacked GO nanosheets can separate contaminants from water via nanosized capillaries, the properties of which, however, might be altered by intercalation of solutes. This study first reports the impacts of common inorganic ions on the structure and separation performance of non-covalently bonded GO membranes. When filtering NaCl, KCl, MgCl₂, CaCl₂, Na₂SO₄, and K₂SO₄ solutions, the flux of GO membranes, fabricated by vacuum filtration, exhibited significant increase over the filtration time in Na⁺ solutions, but maintained stable in the other electrolyte solutions. Rejection decline was observed for all the electrolytes with an order of Na⁺ > Mg²⁺ ≈ Ca²⁺ > K⁺ for the chlorides. X-ray diffraction indicated the GO membrane structure in K⁺ solutions was well maintained and slightly expanded in Mg²⁺/Ca²⁺ solutions over time. However, the ordered structure of GO membranes disappeared after long exposure to Na⁺, explaining the significantly increased flux and reduced rejection. The effect of Na⁺ on the GO membrane structure was ascribed to its relatively large size but weak attraction with GO nanosheets. These findings highlight the importance of introducing strong covalent bonding between GO nanosheets to stabilize the structure and separation performance of GO membranes for water purification.

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1. Introduction

Severe water shortage has motivated the search for alternative freshwater resources such as wastewater, seawater, and brackish

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water because of growing population, industrialization and water pollution [1]. Nanofiltration (NF) and reverse osmosis (RO) membrane processes are extensively applied to produce clean water from these alternative water resources because they can effectively reject contaminants [2]. The currently widely used NF and RO membranes are thin-film composite polyamide membranes, which still have disadvantages such as low water permeability, susceptibility to fouling and chlorine attack [1,3–5]. Therefore, a number of efforts have been made to develop novel membrane materials [4–8].

Graphene oxide (GO) membrane is one class of the emerging membrane materials, which is composed of closely stacked GO nanosheets, a derivative from atomic-thickness graphene partially oxidized on the basal plane or edges [8–15]. GO membranes feature an orderly laminar structure with interconnected nanosized capillaries formed between the stacked GO nanosheets, where water molecules can move extremely fast along the nearly frictionless non-oxidized regions and solutes larger than the capillary size can be excluded [11]. The advantages of GO membranes include the high water permeability due to the frictionless nanosized capillaries and potentially ultrathin membrane thickness [14–17], the ability to be functionalized to achieve particular properties [9], and cheap GO sources [9]. The separation performances of GO membranes for water purification have been broadly explored, including the selectivity of nanoparticles [18–20], small organic compounds [9,12,19–23], heavy metal ions [24], and monovalent/divalent ions [9,12,25–28], as well as the water transport [9,19,23,28–31]. Results suggest GO membranes function at the level of NF [12,18,24,28], validating their potential to be a promising candidate for the next-generation membranes for water reuse and desalination.

GO membranes for water purification are mostly fabricated by vacuum filtration, dip-coating, and layer-by-layer assembly, with or without covalent bonding created by cross-linkers between GO nanosheets [8, 11]. Non-covalently bonded GO membranes [12,18–20,22,23,25–28] are still more studied than covalently-bonded GO membranes [9,21, 24,32] because of the simple fabrication processes. They can maintain their structure via relatively weak van der Waals attraction and hydrogen bonding when in a dry state [33,34]. However, because GO nanosheets with hydrophilic oxygen-containing functional groups are easily hydrated, the structural instability in water of the non-covalently bonded GO membranes has been a major concern about their applications for water purification [8,9,11,33]. Water molecules can hydrate the GO nanosheets and enter the nanosized capillaries, resulting in a significant increase of the interlayer distance (d -spacing) [12,35–37], or even disruption of GO membranes when exposed to harsh physical stress [38].

It should be noticed in addition to water molecules, ions, with hydrated diameters comparable to the d -spacing of GO membranes, can also enter the nanosized capillaries. Ions have been reported to readily interact with GO nanosheets in various manners, e.g. electrostatic interactions with negatively charged carboxyl groups or π -systems, and complexation with carboxyl groups [25–27]. Only a few studies have explored the impact of ions on the GO membrane structure. It has been found that cations able to complex with GO nanosheets (e.g. Al^{3+}) can enhance the structural stability of GO membranes [33,39]. However, the ions enriched in aqueous environment are unable to form complexation, e.g. Na^+ , K^+ , Cl^- , SO_4^{2-} . To date, although there are a few investigations [12,33,35–37,39] on the structural stability of GO membranes due to complex bonding of multivalent ions and hydration by water molecules, it is still unclear whether the intercalation of the ions unable to form complexation into GO membranes and their interactions can induce any changes in the membrane structure. Furthermore, despite concerns about the structural instability of non-covalently bonded GO membranes in aqueous solutions, further investigations on the separation performance over time have not yet been reported.

Here we studied the impacts of intercalation of common inorganic ions on the structure and separation performance of non-covalently bonded GO membranes. Six electrolytes (NaCl , KCl , MgCl_2 , CaCl_2 , Na_2SO_4 , K_2SO_4) as feed solutions were selected to represent the

common ions in aqueous environment, and flux and salt rejection of GO membranes over the filtration time were systematically investigated. The flux and rejection of GO membranes in electrolyte solutions was found to vary over time, dependent on the filtered electrolyte. The variation of the flux and rejection was correlated with the GO membrane structural changes, as indicated by X-ray diffraction (XRD). Particularly, the existence of Na^+ broke down the laminar structure of GO membranes, and thus increased the membrane flux but reduced the salt rejection over time. This study highly suggested stabilizing the structures of GO membranes and monitoring the performance in terms of water reuse and desalination applications.

2. Experimental

2.1. Materials and chemicals

Commercial GO powder was purchased from XFNANO (Nanjing XFNANO Materials Tech Co., Ltd., China). As denoted by the manufacturer, the GO powder has a lateral size of 1–5 μm with a thickness of 0.8–1.2 nm, and the purity is higher than 99%. Polyvinylidene fluoride (PVDF) membranes with a nominal pore size of 0.22 μm (GVVP04700, Millipore, Billerica, MA) were used as the support layer for the GO membrane fabrication. All of the electrolytes tested, including NaCl , KCl , MgCl_2 , CaCl_2 , Na_2SO_4 , and K_2SO_4 , were analytical grade. All the solutions were prepared using deionized (DI) water (ULUPURE, China).

2.2. GO membrane fabrication

GO membranes were fabricated by vacuum filtration. The GO powder was first dispersed in DI water and sonicated for 2 h. Unless otherwise specified, 40 mL of the GO suspension (0.01 mg/mL) was filtered through the PVDF membrane (filtration area 14.5 cm^2) under -0.8 bar at room temperature, forming the GO membrane composed of a thin GO layer on the PVDF support. The resultant GO membrane was vacuum-dried (-0.95 bar) at 40 $^\circ\text{C}$ for 40 h.

2.3. GO membrane characterization

The fabricated GO membranes were characterized by Fourier transform infrared (FTIR) spectroscopy (Vertex 70, Bruker, Karlsruhe, Germany), zeta potential analyzer (Zetasizer Nano ZS90, Malvern Instruments, UK), scanning electronic microscopy (SEM, Hitachi S4800, Japan), and XRD (Bruker D8 Advance, Karlsruhe, Germany). The reagent for zeta potential analysis was composed of 1 mM NaCl and 50 mg/L polystyrene (the tracer for zeta potential analysis denoted by the manufacturer).

The d -spacing of dry and wet GO membranes were calculated by XRD [12,35,36,40]. Scanning was conducted with focused $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at a scan rate of $3^\circ/\text{min}$, for 2θ from 5° to 25° . The wet GO membranes were prepared by immersing the membranes in DI water or the electrolyte solutions (NaCl , KCl , MgCl_2 , CaCl_2 , Na_2SO_4 , K_2SO_4). A newly fabricated GO membrane was used for each testing condition (i.e. a certain solution with a predetermined immersing time). The immersion time in DI water was 1 h to 24 h. For the cases of electrolyte solutions, the GO membranes were first immersed in 10 mL of DI water for 2 h, and then the electrolyte stock solutions were separately spiked to reach an ionic strength of 3 mM. The immersion time in electrolyte solutions was 1 min to 24 h.

Considering the interference of water molecules on the membrane surface with XRD signals and the state conversion (wet to dry) of GO membrane, a tailored protocol was developed for the wet GO membrane measurements. Scanning was performed immediately on the wet GO membranes after taken out from the solution, and repeated 3 to 4 times with no time intervals in between until the characteristic diffraction peak of dry GO membranes appeared. The scanning curve with

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