Synthesis of graphene oxide membranes and their behavior in water and isopropanol

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A B S T R A C T

Graphene oxide (GO) membrane has been synthesized on commercial polysulfone ultrafiltration membranes (Pore size: 17 nm) using the drop casting method followed by baking at 90 °C for 24 h. Baking resulted in the reduction of GO and removal of bulk water intercalated in the GO sheets. Deposited GO film showed high stability under shear stress variation. This work shows that water adsorption on the GO membrane determines its permeation performance. Despite the higher viscosity of isopropyl alcohol (IPA), its permeability was 7 times higher than water through the baked ("dry") GO membranes, which were never contacted with water. However, IPA permeability of GO membranes dropped to 44% (of deionized water) when contacted with water ("hydrated" or "wet" GO membranes). Extensive size exclusion (rejection) studies with various dye and dendrimer molecules showed pore size reduced from 3.3 nm in the "dry" state to 1.3 nm in the "wet" state of GO membranes. FT-IR characterization of GO membrane suggested adsorption of water on the nanochannels of the active layer. Also, significant decay in flux was observed for water (82% of its initial flux) as compared to IPA (38% of its initial flux) for initially dry GO membranes.

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1. Introduction

Graphene-based materials have shown immense potentials for energy storage, metal free catalyst for fuel cells and advanced oxidation, along with the separations ranging from gas phase to water based systems [1–7]. Incorporation of Graphene Oxide (GO) on membrane surface or in the polymer matrix has demonstrated improved membrane properties, such as water permeance, anti-fouling and antimicrobial, solvent resistance, thermal and mechanical stability [8,9]. GO membranes have the capabilities to separate small organic molecules, divalent ions and gas phase separations. Thermal and solvent resistance of GO membranes enable them to work in certain cases, such as solvent based separations and fluids at elevated temperature, where application of polymeric membranes are limited due to thermal stability and solubility of polymer in solvent [10]. Simulation and experimental studies have demonstrated faster transport of water through monolayer of graphene, thus identifying the capabilities for more energy efficient separations [11–14]. However, the complexities involved in the synthesis of monolayer graphene membranes limited their practical realization. GO membranes on the other hand, can be easily fabricated on porous substrates by stacking multiple GO sheets, using the process of drop casting, vacuum filtration, and doctor blade, giving it an edge over monolayer graphene and other polymeric nanofiltration membranes [15–18]. The nanoscale dimension of the corridor for flow of fluid in GO membranes results in the slip of fluids at the interface, leading to a higher permeation rate than the predictions from the Hagen poiseuille equation [14,19,20]. Fast water transport along with the other aspects such as, ease of fabrication, separations on nanoscale (size), mechanical, thermal and solvent resistance make GO membranes a promising candidate for nanofiltration (NF) and have attracted attention of membrane community.

Graphene oxide is a two-dimensional nanomaterial, with the domains of sp^2 hybridized carbon atoms arranged in a honeycomb structure decorated with domains of oxygen containing functionalities such as carboxyl, carbonyl, epoxy and hydroxyl attached to

Abbreviations: NF, Nanofiltration; UF, ultrafiltration; GO, graphene oxide; NR, neutral red; R6G, Rhodamine 6G.
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the sp³ carbon, on the basal plane. π-π interactions of sp² hybridized domains and hydrogen bonding through some of the oxygen containing functionalities gives it structural integrity, holding it in a laminar structure [21]. The GO membrane has a complex microstructure consisting of channels between two GO sheets, inter-edge spaces, and wrinkles. Several molecular dynamic studies have investigated the transport mechanism of water through this complex microstructure. Studies indicate that transport of water is fast through the sp² domains of GO, but limited by slower water transport in the sp³ domains [14]. It is also speculated that wide channels formed at wrinkles and inter-edge spaces are the major route for transport of water through the GO membranes. An interesting experimental demonstration by Gao's group showed narrowing of wrinkles on the GO membrane decreasing water flux with time at a constant pressure suggesting the importance of wrinkles in the transport of water [22]. As such, the study of GO membranes is still an emerging field and research to understand the atomic structure, transport mechanism, and separation mechanism is in progress [23–29].

The permeability of these membranes has shown different responses to the operating conditions compared to polymeric membranes. XRD studies have shown an increase in interlayer distance from 7.7 Å to 12.09 Å of GO when exposed to humid air suggesting hydration of GO membranes [20]. Any change in dimensions of the nanochannels would result in dramatically different rates of transport of fluids through the GO membranes. For example, Huang et al. noted the decline in water flux for GO membranes with increasing ionic strength using NaCl [30]. Declining water flux was reported likely due to the screening of negative charge on the GO surface, resulting in less repulsion force between the GO sheets reducing the interlayer spacing. Pressure normalized flux for these membranes also reduced with increasing operating pressure, suggesting the narrowing of nanochannels under pressure. Furthermore, interactions of solvents with GO and their role in determining the permeability through GO membranes is also critical for solvent based applications [31]. Shi et al. observed a decrease in permeation of water while increasing oxidation extent of the GO, likely due to a higher degree of hydrogen bonding [32]. Water can form a stable adsorbates on the GO surface which has been observed to narrow the capillaries for flow of the fluids. This led to improved selectivity of GO membranes for gas phase separations [3,33]. Thermodynamic simulations performed by Korobov et al. suggest the different extent of intercalation of various solvent molecules in GO nanochannels [34]. Due to these differences in interactions, it may not be possible to predict the performance of GO membranes with organic solvents from their performance with aqueous solutions.

In this study, GO membranes were fabricated using the drop cast technique on commercial polysulfone ultrafiltration membranes. GO membranes were characterized by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Contact angle, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) to establish the chemical state of GO in the membranes. Permeation and rejection performance of the GO membranes was measured for IPA and water as solvents. Our findings suggest that water adsorption on the GO surface is a critical factor that controls the flux and sieving effect of the GO membrane. For GO membranes, the previous history of contact with water or highly hydrophilic molecules is a major factor for their performance.

2. Experimental

2.1. Materials

Aqueous dispersion of Graphene Oxide (4 mg/ml) was purchased from Graphenea, Inc. PS35 (ultrafiltration membrane) and Dow NF270 (nanofiltration membrane) was supplied by Nanostone water Co. and Dow Flimtech, respectively. Reagent grade isopropanol, magnesium sulfate, ferricyanide ($[Fe(CN)_6]^{3-}$), rodamine B labeled polyethylene glycol with molecular weight of 5000 g/mol, FITC labeled polyethylene glycol with molecular weight 2000 g/mol, Tris(4-carbazoyl-9-ylphenyl) amine and humic acid were purchased from Sigma-Aldrich. All reagents were used as received. Water used at all stages of the experiments was purified (final resistivity <18.2 MΩ, TOC<1 ppb) using a Purelab flex water purifier obtained from ELGA Lab water.

2.2. Preparation of GO-PS35 membranes using the drop-cast method

GO membranes were fabricated using aqueous GO suspension (4 mg/ml) on commercial ultrafiltration membrane PS35. PS35 has a 30 μm thick polysulfone layer having a mean pore size of 17 nm on a 150 μm thick polyester support. Before using, the PS35 films (10 × 10 cm²) were first rinsed with deionized water to remove residual glycerol on top of it. After drying in air, dropwise deposition of 0.2 mg/L GO suspension on the surface of PS35 was carried out to get a loading of 120 mg/m². The PS35 membrane has some hydrophilicity due to the presence of additives (Polyvinylpyrrolidone), which helped in spreading of suspension and formed a thin film of GO on the PS35 surface. GO suspension deposited on PS35 membranes was dried in stagnant air. Air dried GO on the PS35 film was then incubated in the oven at 90 °C for 20 h. GO coating on the PS35 film turned gray from light brown after incubation (Fig. S1). The composite film of GO and PS35 is referred as GO-PS35 membrane henceforth.

2.3. GO-PS35 membrane performance measurement

The Sterlitech dead-end cell and the Sterlitech cross-flow cell were used to measure permeation of fluids and rejections of solutes. Dead-end filtration cell had an active filtration area of 13.2 cm². Permeation rate measurements of fluid were carried out by monitoring the mass of permeate through the RS232 output of weighing scale at a sampling rate of 50 sec⁻¹. Crossflow setup required a rectangular piece of membrane with an active filtration area of 20.6 cm². Temperature of the working fluid was controlled at 24 °C in the crossflow setup. The flux was measured by recording the volume of permeate collected over 5 min at an interval of 2 h during the experiment. Flow diagram for the experimental setup is shown in Fig. S3.

2.4. Rejection measurement

The rejection (R) is defined as follow,

$$R = \left(1 - \frac{C_{per}}{C_{feed}}\right) \times 100,$$

where C_{per} is the concentration of the permeate and C_{feed} is the concentration of the feed solution. The permeate and feed concentrations of the $K_3Fe(CN)_6$, Neutral Red and FITC-labeled PEG solutions were measured with the UV–Vis spectrometer at 302 nm, 530 nm, 525 nm, respectively. During measurements, 250 ml dye solutions were filled in the batch cell. The permeate concentration was sampled after passing 30 mL of dye solution through the GO membrane. Also, rejection tests were carried on three independently synthesized GO membranes and measurements were repeated three times on the same piece of membrane each time to