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Synthesis of graphene oxide membranes on polyester substrate by spray coating for gas separation

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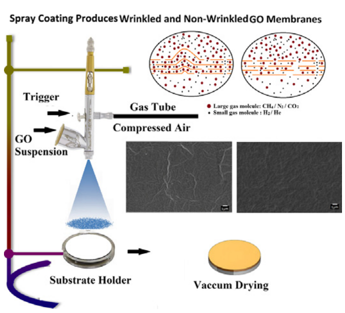
HIGHLIGHTS

- High quality GO membranes can be coated on polymer substrate by spray coating method.
- Prepared GO membranes offer gas characteristics similar to those made by filtration.
- Dilute GO suspension in spray coating reduces the formation of extrinsic wrinkles.
- Less wrinkles results in reduction in the porosity of inter-layer galleries.
- Less wrinkles leads to higher selectivity of H_2 over large gas molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene oxide (GO) membranes have shown promising gas separation characteristics specially for hydrogen showing potential for industrial applications. However, GO membranes made by filtration, the most common synthesis method, contain wrinkles affecting their gas separation characteristics and the method itself is difficult to scale up. In this work, high quality GO membranes are made from GO suspension by easily scalable spray coating technique (and also by filtration method for comparison) on hydrophilic polyester track etch substrates. GO sheet suspensions of large sheet average size (33 μm) and dilute concentrations are used to minimize GO sheet edge-to-edge interactions and minimize extrinsic wrinkle formation. Single gas permeation and separation experiments of equimolar H_2/CO_2 binary mixture were conducted to evaluate the permeation and separation characteristics of prepared membranes. GO membranes prepared by spray coating offer gas characteristics similar to those made by filtration, however using dilute GO suspension in spray coating reduces the formation of extrinsic wrinkles causing reduction in the porosity of the inter-sheet pathway where the transport of large gas molecules dominates. This study demonstrates an efficient, scalable and cost-effective approach for synthesizing large area GO membranes with enhanced hydrogen separation.

1. Introduction

Graphene oxide (GO) is a unique material that can be viewed as a single layer of graphite with various oxygen containing groups spread on the sheet basal planes and edges (Lerf et al., 1998). Membranes prepared by stacking GO sheets have shown attractive gas separation characteristics specially for hydrogen (Li et al., 2013; Chi et al., 2016), that make them of interest for large-scale industrial applications. Filtration is the most commonly used method to prepare stacked GO membranes with good control over membrane thickness (Huang et al., 2014). However, extrinsic wrinkles

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were observed in GO membranes made by filtration (Chi et al., 2016; Dikin et al., 2007; Ibrahim and Lin, 2018; Klechikov et al., 2015) and the method itself is difficult to scale up for cost-effective production of large area GO membranes.

Wrinkling is a common phenomenon in 2D films and membranes. Graphene sheets are not perfectly flat and TEM studies showed that graphene is microscopically corrugated (Meyer et al., 2007). Further atomistic simulation studies show that such ripples with an amplitude of about 1 Å were intrinsic (Fasolino et al., 2007). GO is more susceptible to intrinsic corrugations due to thermal fluctuations and stresses during oxidation, attached functional groups (Zheng et al., 2010) and structural defects (Liu et al., 2011). Unlike the atomic or nanometer level wrinkles in monolayer graphene oxide sheets, the undulations seen in GO membranes normally have much higher amplitudes and seems to affect the GO membrane performance. Higher H_2 permeance and lower H_2/CO_2 separation factor (51 vs 240) of GO membranes made by filtration compared to membranes made by spin coating using the same GO suspension, was attributed to the formation of extrinsic wrinkles in the membranes made by filtration (Chi et al., 2016). Wei et al. (2016) showed that GO channels under wrinkles are larger than those under the flat area which reduce the resistance to water permeation in GO membranes. They also found that GO wrinkles became narrower and water flux decreases under the influence of hydraulic pressure during filtration.

Some efforts were done to analyze the reasons for the formation of wrinkles in graphene based membranes. Wrinkles were observed in large-area, few-layer graphene grown on a polynickel substrate under optimized CVD conditions (Chae et al., 2009). It was proposed that the wrinkles were formed by two processes: (i) nucleation of defect lines on step edges between Ni terraces and (ii) thermal-stress-induced formation of wrinkles around step edges and defect lines. Wei et al. (2016) showed that the formation of wrinkles on the surface of GO membranes originates with the formation of slender initial wrinkles that gradually grow with the deposition of GO sheets. Initial wrinkles could form due to GO sheet wrinkle, sheet folding or stacking. They also demonstrated that the formation of GO sheet wrinkles originates due to the water accumulating between the substrate and the soft GO sheets. The water drains gradually and a wrinkle is formed when the GO sheet contacts the substrate. Also, Kim and coworkers (Shen et al., 2014) showed that GO sheets placed in the edge-to-edge arrangement tend to buckle due to hydrogen bonding between the edges. GO sheet interactions and water accumulation between the substrate and GO sheets cannot be avoided in membrane synthesis by filtration.

Jin and co-workers (Guan et al., 2017) used spray coating to fabricate GO membranes on alpha-alumina substrates for gas separation offering promising results for scalable GO membrane synthesis. Their study focused on the effect of evaporation rate on GO stacking during the whole assembly process by controlling the volume of ethanol to water in GO suspension. Although, alpha-alumina substrates are mechanically strong, they are expensive and difficult to scale up for production of membrane modules with high packing density.

To fully explore the scalability of spray coating method for GO membrane synthesis, GO membranes should be deposited on cost-effective, easily scalable polymer substrates. In this work, we combine GO membrane synthesis using scalable spray coating method on a scalable, planar polymer substrate. Since GO nanosheets can be cheaply produced in a large scale by oxidation and exfoliation of graphite (Sun and Fugetsu, 2013), the obtained results could demonstrate a cost-effective scalable approach for GO membrane synthesis for large area industrial gas separation applications. Furthermore, we expect spray coating method to produce GO membranes with less wrinkles and thus better separation characteristics due to the following reasons. Using dilute concentration GO suspensions in spray coating may decrease GO edge-to-edge interactions since each spray disperses a few number of GO sheets on the substrate at a larger distance between the sheets. Also, the solvent in spray coating evaporates as it reaches the substrate different from the drainage system of the solvent in filtration. The objective of this work is to evaluate the synthesis and gas separation properties of GO membranes by spray coating on scalable polyester track etch (PETE) substrates, compare the structure and properties of these GO membranes with those obtained by the filtration method with focus on analyzing the effect of extrinsic wrinkles on membrane performance.

2. Experimental

A modified Hummers' method (Hummers and Offeman, 1958) was applied for the synthesis of GO sheets as reported in our previous publication (Ibrahim and Lin, 2018). Typically, 100 ml of concentrated sulfuric acid, (H_2SO_4, EMD Millipore, SX1244, 95.0–98.0%) was charged into a flask equipped with a Teflon mechanical stirrer. The flask was cooled down to 0 °C using an ice bath. 2 g graphite flakes (Sigma-Aldrich, SKU: 332461, ~150 μm flakes) were added to the flask under stirring followed by 1 g sodium nitrate ($NaNO_3$, Alfa Aesar, ACS, 99.0%). 5 min later, 12 g of potassium permanganate ($KMnO_4$, Alfa Aesar, ACS, 99.0%) was slowly added in small doses to the mixture under stirring. The whole mixture was then stirred for 30 min then the ice bath was replaced by tap water bath and heat was supplied to keep the temperature at 40 °C while stirring continued for 5 h. After that, 100 ml of deionized water was slowly added to the flask raising the suspension temperature to 98 °C. The mixture was further stirred at this temperature for 15 min with no external heat and subsequently diluted with 300 ml deionized water and 6 ml hydrogen peroxide (H_2O_2, Sigma Aldrich, 35 wt.%). The washed and vacuum dried GO powder was sonicated in ethanol for 30 min to achieve sheet exfoliation and prepare 2 mg/ml GO suspension in ethanol.

Polyester track etch (PETE) substrates (Sterlitech, SKU: PET0125100) were used as the supports for coating GO membranes. The substrates containing pores of 0.1 μm in pore diameter were 10 μm in thickness and 25 mm in diameter. To investigate the effect of sheet stacking method on the quality of the membrane, GO membranes were synthesized in this study by vacuum filtration and spray coating method. For GO membrane fabrication by filtration, the prepared GO suspension (2 mg/ml in ethanol) was further diluted with water to a concentration of 0.002 mg/ml. A home-made vacuum filtration system was used to deposit the desired volume of GO suspension onto PETE substrate. Details in vacuum filtration synthesis of GO membranes was described elsewhere (Ibrahim and Lin, 2018).

For spray coating, GO suspension (2 mg/ml in ethanol) was diluted using 50:50 vol.% water-ethanol mixture to prepare suspensions of concentrations 1, 0.5 and 0.1 mg/ml. GO suspensions were vertically sprayed onto PETE substrates using a gravity feed airbrush (Talon Dual Action Airbrush, TG 208 from Paasche-USA). The airbrush has a head size of 0.38 mm and assembled with air as a carrier gas, as shown in Fig. 1 and Fig. S1. The peripheral of the polyester substrate was secured on a Polypropylene petri dish during spraying process using adhesive tape. The inlet pressure of air was regulated at 50 psi. The airbrush tip was placed vertically at 15 cm from the substrate and thus the tiny droplets of the sprayed solution covered the entire cross section of the mounted substrate. Spray deposition was carried out for ~2 s, and a rest period of 5 s was given for the solvent to evaporate by the air continuously coming out of the airbrush. As spray deposition continues, the coating grows to form a continuous GO film covering the pores of the PETE