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Aldehyde functionalized graphene oxide frameworks as robust membrane materials for pervaporative alcohol dehydration

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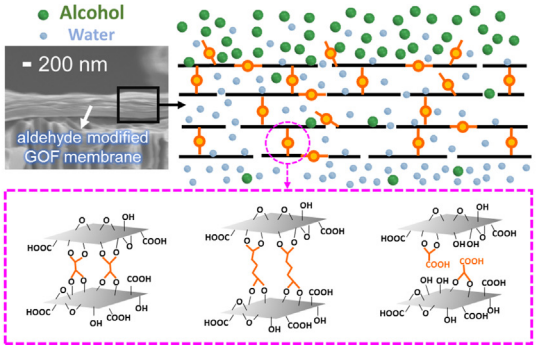
HIGHLIGHTS

- Three aldehyde functionalized GOF membranes have been molecularly designed.
- The resultant GOF membranes displayed adjustable microstructures.
- GOF membranes exhibited greatly improved alcohol dehydration performance.
- Excellent long term stability was found for the GOF membranes within 160–200 h.

GRAPHICAL ABSTRACT

Graphene oxide framework (GOF) membranes functionalized by three different aldehydes show adjustable microstructures, improved separation performance and good stability.



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ABSTRACT

To glue the graphene oxide (GO) nanosheets more firmly and to fabricate more stable GO membranes for long-term applications, three types of graphene oxide framework (GOF) membranes have been molecularly constructed *via* the aldehyde-functionalization of GO and a pressure assisted ultrafiltration method. The resultant GOF membranes not only possess GO/aldehyde covalent bonds but also display adjustable microstructural properties, confirmed by FTIR, XPS, XRD and positron annihilation spectroscopy (PAS). All aldehyde modified GOF membranes exhibited much improved separation performance for ethanol dehydration *via* pervaporation, as compared with the pristine GO membrane. The GOF membranes were also tested for the dehydration of ethanol, isopropanol, and *n*-butanol at different feed temperatures. Excellent separation performance at 60 °C for *n*-butanol dehydration was obtained with a high flux of 2593 g m^{-2} h^{-1} and the water concentration in permeate of 99.7 wt%. Importantly, the pervaporation stability of GOF membranes at a relatively high temperature was investigated for the first time. The membranes performed well for the dehydration of alcohols at 60 °C within a long period of 160–200 h.

1. Introduction

In recent years, graphene and its oxidized derivative graphene oxide (GO) have become promising membrane materials due to their easy accessibility, excellent chemical stability, and good mechanical properties (Geim and Novoselov, 2007; Geim, 2009;

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Dreyer et al., 2010; Kim and Nair, 2013; Huang et al., 2014). Similar with graphene, GO is a two-dimensional material which can be only one-atom thick with a lateral dimension of several hundred nanometers. Therefore, the GO nanosheets could be stacked and assembled easily with specific applications (Chen et al., 2009; Smith and Freeman, 2014). More importantly, due to its oxygen containing functional groups (*i.e.*, hydroxyl, carboxyl, carbonyl and epoxy groups), GO has more attractive characteristics than graphene, such as better dispersion in water (higher hydrophilicity), and adjustable micro- and meso-structures because of easy functionalization *via* chemical modification. Accordingly, a variety of GO based membranes have been made for gas separation (Yang et al., 2013; Kim et al., 2013; Li et al., 2013), pervaporation (Huang et al., 2014; Lou et al., 2014; Hung et al., 2014a, 2014b; Tang et al., 2014; Li et al., 2014; Chen et al., 2015) and ultra/nanofiltration (Hu and Mi, 2013; Huang et al., 2013; Xu et al., 2013; Zhang et al., 2015, 2016; Xu et al., 2016), etc.

In 2012, Nair and his co-workers demonstrated that GO membrane could completely impede the permeation of liquids and vapor including helium, but allow rapid permeation of water vapor (Nair et al., 2012). This encouraging finding indicated that GO has great potential in the pervaporation field for the dehydration of organic solvents due to its hydrophilicity and suitable packing channels for water transport. Since then, the utilization of GO for pervaporation grew fast (Huang et al., 2014; Lou et al., 2014; Hung et al., 2014a, 2014b; Tang et al., 2014; Li et al., 2014; Chen et al., 2015). Most of them prepared GO membranes without any modification. The resultant GO membranes had a relatively low selectivity or low flux due to the unsatisfied packing and large membrane thickness (Lou et al., 2014; Hung et al., 2014b). In addition, the long term stability of these GO membranes for pervaporation was not studied. The van der Waals attractive force was the main driver to assemble these pristine GO nanosheets into membranes. By means of chemical modifications with covalent bonds, one may be able to glue the GO nanosheets more firmly and fabricate more stable GO membranes for long-term applications.

Hung et al. were pioneers in studying the chemical modified GO framework (GOF) membranes for pervaporation (Hung et al., 2014b). They found that the d-spacing of the GO structure (*i.e.* the layer-to-layer distance of GO nanosheets) could be tuned by using different diamines. In addition, the ethylenediamine cross-linked GOF membrane exhibited a greatly improve separation factor with an excellent flux as compared with pristine GO membranes. Inspired by their encouraging findings, we aim to further develop more functionalized GOF membranes with various tunable microstructures *via* covalent chemical modifications.

Currently, several types of chemicals have been reported to modify GO materials such as amino acids (Bourlinos et al., 2003), diaminoalkanes (Hung et al., 2014b; Zhang et al., 2015; Bourlinos et al., 2003; Herrera-Alonso et al., 2007; Stankovich et al., 2010), boronates or boronic acids (Bourlinos et al., 2003; Burress et al., 2010; Srinivas et al., 2011), acyl chlorides (Hu and Mi, 2013), isocyanates (Zhang et al., 2009) and aldehydes (Nantao et al., 2011; Tan et al., 2013), etc. Generally, the existence of active oxygen containing group on the GO layers are responsible to the chemical reactions, which result in the formation of additional new functional groups. However, most reported studies emphasized on the functionalization of GO to improve its mechanical properties, hydrophobicity or sorption properties, only a few studies focused on the enhanced separation performance by the functionalized GOF membranes (Hung et al., 2014b; Zhang et al., 2015).

Therefore, we aim to design and fabricate GOF membranes in this work by using various aldehydes for pervaporative alcohol dehydration. Aldehydes are chosen as the modifiers because they are highly reactive in various chemical reactions. For example, aldehydes have been reported to react with amines via imine or enamine condensation (Sprung, 1940; McMurry, 2011; Hua and Chung, 2015). Besides, they can also react with hydroxyl groups to form either hemiacetals or acetals. Thus, they also serve as cross-linkers to modify pervaporation polymeric membranes containing hydroxyl groups such as poly vinyl alcohol, chitosan, alginate, and cellulose (Chapman et al., 2008; Feng and Huang, 1997; Shao and Huang, 2007; Bolto et al., 2009). Even though GO papers cross-linked by glutaraldehyde have been fabricated (Nantao et al., 2011; Tan et al., 2013), previous studies only focused on the reaction mechanism and the improvement of mechanical strength. Therefore, a large room remains open for researchers to explore aldehyde functionalized GOFs in terms of membrane formation and potential separation applications. Three aldehydes are chosen in this work to modify GO, including glyoxal, glutaraldehyde and glyoxylic acid. Fig. 1 shows their structures and their resultant GOFs.

To fabricate GO or GOF membranes, several methods are available in literatures including evaporation (Chen et al., 2009), vacuum filtration (Huang et al., 2014; Dikin et al., 2007; Putz et al., 2011) or pressure-assisted filtration (Hung et al., 2014a; Tang et al., 2014; Zhang et al., 2015), dip coating (Lou et al., 2014), spin coating (Robinson et al., 2008), or Langmuir-Blodgett

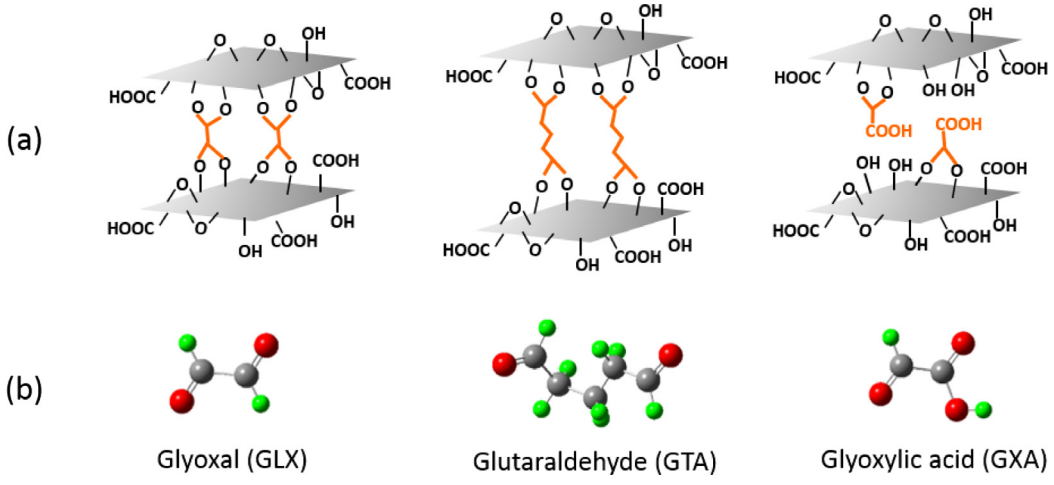

Fig. 1. (a) Structural diagrams of GOF membranes (GO-GLX, GO-GTA, and GO-GXA). Each GOF was functionalized by using a special aldehyde. (b) Molecular structures of GLX, GTA, and GXA. Green, red, and grey spheres represent H, O, and C atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)