Membranes for water purification

Abstract

At present, a significant progress has been achieved in the field of water filtration, in this regard, membrane technology has played a crucial role. Membrane technology is a rapidly growing research area with several real times applications such as gas and aqueous purification. Notably, there are already some well-established membranes for these applications, however, their accuracy, ability, and cost effectiveness vary depending on membranes' type. The focus is on the design and fabrication of the membranes, membranes preparation condition, and membranes' physicochemical properties on separation performances.

Keywords: Membrane, Filtration, Purification, Water.

1. Introduction

Water treatment in gas and aqueous phases with membrane separation has attracted great attention. Reasons include growing water-use from population shifts and complex land-use patterns that require abundant water and heavier request from industry and energy production. Considering the need for water purification, technologies that can efficiently separate ions and molecules of water are highly desirable. In particular, these technologies aim to develop such water-based membranes for maximum separation efficiency and exceptional permeance. Ideally, an efficient membrane should be able to maximize the water permeance, to be robust enough to resist the applied filtration pressure, and to have a narrow distribution of pore size for excellent selective separation. Owing to the excellent mechanical property, chemical stability, and availability of rich functional groups, graphene-based materials are widely being researched for membrane application. To this end, numerous efforts have been made to fabricate graphene-based membranes.

The filtration concept utilizes graphene-based membranes for separation of ions and molecules from aqueous solutions. Polymeric nanofiltration membranes are emerged as a promising method for filtration on the laboratory scale [*J. H. Hanemaaijer et al., Journal of Membrane Science, 1989, 40, 199–217*]. Although polymeric membranes are widely used due to their low cost, they have limitations. [*G. M. Geise et al., Polymer Science Part B: Polymer Physics, 2010, 48, 1685–1718*]. The limitations associated with the use of polymeric membranes can be possibly overcome with the use of graphene-based membranes.

This study aims to investigate recent developments with respect to the design and fabrication of graphene-based membranes for water filtration application. In this regard, membrane synthesis methods, membranes preparation condition, membranes' physicochemical properties on separation performances are discussed.

2. Graphene oxide (GO) membranes

A perfect molecular level separating unit for any kind of species to be filtered is on very high demand. In recent years, GO has emerged as an important material which can filter ions and molecules as a membrane. A membrane is considered as a barrier with an ability to allow the passage of certain species while blocks other depending on characteristics of the membrane and species to be filtered. GO—partially oxidized and stacked sheets of graphene—is a type of two-dimensional nanomaterial with a single-atom thickness. GO sheets include pristine regions, oxidized regions, and a small portion of holes [*D. An et al., Industrial and Engineering Chemistry Research, 2016, 55, 4803−4810*].

Due to a large number of surface functional groups, GO sheets can be stacked on top of each other to form a uniform laminar structure with a well-defined interlayer space [*J. Y. Chong et al., Journal of Membrane Science, 2018, 549, 385-392*]. Tunable interlayer spaces within lamellar GO membranes offer a more straightforward approach which controls ions and molecules passage and show a potential in separation applications. The unique physicochemical properties of GO notably its exceptionally high surface rea and mechanical strength can lead to improved technologies which addressing global environmental challenges. The use of GO in membrane applications is particularly attractive because they are easy to fabricate, mechanically and chemically robust, and can be amenable to industrial-scale production.

The whole structure of GO includes two parts in terms of functionality and participation in reactions: the sp^3 functional oxidized regions and the sp^2 pristine (graphitic) regions (**Figure 1**) [*W. S. Hung et al., Carbon, 2014, 68, 670-677*]. High resolution TEM imaging also reveals other features such as nano-sized holes and small atomic defects in layers of GO [*J. H. Hanemaaijer et al., Journal of Membrane Science, 1989, 40, 199–217*]. The oxidized graphene sheets, GO, acquire multiple defects and the degree of the defects is subject to the additive amount of oxidant and the oxidizing time. The high defect density introduced in the carbon structure significantly lowers the electronic and mechanical properties of graphene. The oxygen functionalities make GO a hydrophilic material which forms stable suspensions in aqueous media.

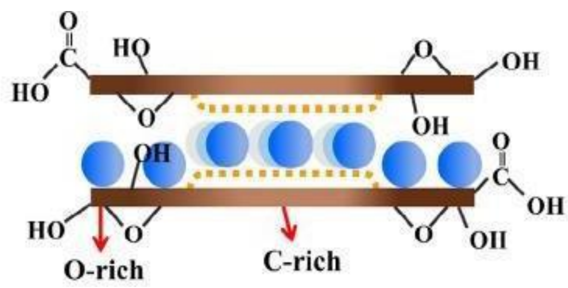

Figure 1. The GO sheets illustrating the hydrophilic O-rich edge, to which H_2O molecules are adsorbed, and the hydrophobic C-rich central region, where there is a low-fiction channel (dashed lines) of monolayer H_2O molecules.

The structure of membrane contains a number of GO sheets with lateral size “L”. The functionalized regions act as spacers that keep adjacent GO sheets apart and also prevent them from being dissolved. The pristine regions provide a network of nano-capillaries (commonly termed as “d spacing”) between the GO sheets to provide passage for molecules and ions to diffuse in the direction parallel with the GO sheets (**Figure 2**) [*Yue-Heng Xi et al., Applied Materials and Interfaces, 2016, 8, 15557-15566*]. This d spacing is defined as the center to center distance between two adjacent GO sheets and allows nearly frictionless flow of water molecule layers.

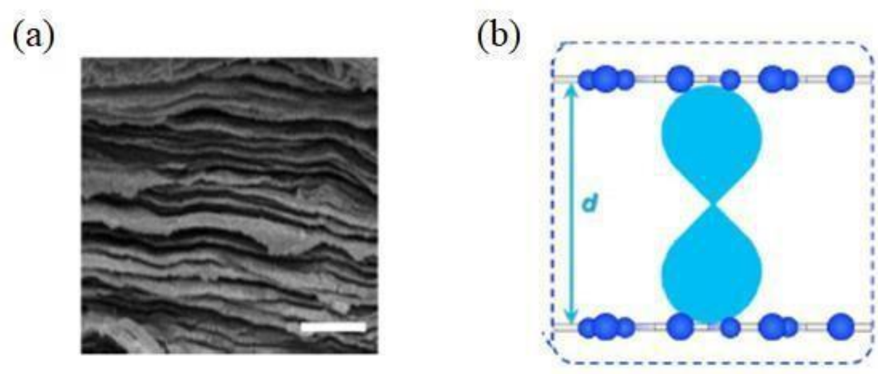

Figure 2. (a) Electron micrograph of the GO film’s cross-section and (b) Schematic view for possible permeation through the GO laminates with lateral size and interlayer space “d”.

GO membranes consist of many stacked layers of GO with an interlamellar spacing of 0.6 - 1.1nm depending on, amongst other things, the degree of hydration. The d spacing between the GO sheets under various relative humidity environments was measured by Liu *et al*. using XRD [*R. Liu et al., Scientific Reports | 7: 9761 | DOI:10.1038/s41598-017-09777-y*]. Exposing the GO membranes to water vapor results in a shift in the (001) reflection, which corresponds to an increase in the d spacing. The d spacing was calculated by Bragg's law: $\lambda = 2d \sin(\theta)$ where λ is the wavelength of the X-ray beam (0.154 nm), d is the distance between the adjacent GO sheets, and θ is the diffraction angle of (001) peak. Because of the existence of oxygen-containing functional groups on GO sheets, the d spacing of the GO membrane composed of stacked sheets is ∼6−7 Å under dry conditions, which is larger than the d spacing of graphite of 3.4 Å. As the humidity increases, more water molecules diffuse into the interlayer between GO sheets and d spacing increases accordingly. Therefore, to achieve full potential of GO membranes for high separation performances, d-spacing must be accurately characterized.

The microstructures of GO membranes such as stacking of GO sheets is another important variable affecting GO membranes' compaction. Assembly plays a critical role in the structure-properties relationship of the GO membranes, which in turn controls membranes' separation performances. The membrane microstructure is shown to be affected by membranes preparation methods. GO membranes can be easily fabricated via different methods such as filtration-assisted method, casting/coating, and layer-by-layer (LbL) assembly method. The resulting GO laminates possess excellent mechanical strength due to the strong interlayer hydrogen bonds between adjacent GO layers that hold all the flakes tightly. Compared with filtration-assisted methods, fabricating membranes from the latter is technically challenging and have several disadvantages as described in **Table 1**. The proposed disadvantages severely restrict their promising applications in the GO membranes fabrication [*J. Ma et al., Membranes, 2017, 7, 52, doi:10.3390/membranes7030052*].

Table 1. GO membranes preparation methods.

Method	Description	Disadvantage
Casting/coating based	Drop-casting Dip-coating Spray-coating	Nonuniform deposition of GO nanosheets and poor control over the membrane thickness
LbL assembly	Layer by layer assembly	Not easily scaled-up or energy efficient

In contrast, filtration-assisted methods allow reasonable and easy control over the membrane thickness and microstructure, changed by adjusting concentration and volume of the GO dispersion. Vacuum filtration-assisted method is where aqueous-dispersed GO strongly interacts with a hydrophilic and most commonly used porous media, namely anodized aluminum oxide (AAO) filter paper [*C. N. Yeh et al., Nature Chemistry 2015, 7, 166-170*]. This method results in the formation of a semi-ordered arrangement of the GO layers. In this method, an aqueous dispersed GO strongly interacts with AAO filter discs and strong interaction between hydroxyl and carboxyl groups of GO and AAO filter disc results in the formation of GO membranes with improved mechanical strength. Therefore, vacuum filtration is a potential route for large-scale preparation of the GO membranes, which produces highly stable GO-like lamellar films in water.

Different possible separation mechanism of GO membranes for nanofiltration have been illustrated by literature. Taking the aqueous phase and vapor phase separations as examples, three possible separation mechanisms have been identified within GO membranes [*Y. Zhang et al., Current Opinion in Chemical Engineering 2017, 16, 9–15*]. The selectivity can be achieved by the following mechanisms: size exclusion from the interlayer space of the GO membrane, electrostatic interaction between different ions and negatively charged GO sheets and ion adsorption through the diverse interactions of ions with different regions on GO sheets. Because of size exclusion from the d spacing within the GO membrane, molecules and ions can be separated according to their hydrated radius. The effective volume occupied by an ion in water is characterized by its hydrated radius. In addition to the hydrated radius of ions, both ion charges and its interaction with GO sheets affect the separation performance of the GO membrane. Different anions and cations exhibit different permeation properties through the GO membrane. Carboxyl and hydroxyl groups on GO sheets are ionized in water, which makes the GO sheets negatively charged. This affects the mobility of ions with different electric charges. Finally, separation is achieved by ion adsorption including cation-π interaction and metal coordination to GO sheets. This mechanism indicates that transition metallic cations prefer to interact with the sp^3 C–O matrix via coordination interactions, whereas alkali and alkaline-earth cations prefer to interact with the sp^2 clusters within the GO sheets via cation-π interactions.

The preparation process of the GO membrane can influence greatly the separation performance. The separation performance of GO membranes can be adjusted by changing thickness, lateral sheet size, and degree of oxidation. Two types of pores inside GO membranes can control ionic and molecular transport and the type of which critically depends on the membranes' thickness. Membrane thickness is controlled by changing the concentration and volume of the GO dispersion used for its preparation. Ions and molecules transport pathways in the relatively thin membranes are mainly through pores created by vacancies, holes, and voids formed within individual GO sheets. Also, interconnected interlayer spaces as slit pores formed by stacked GO sheet is dominant only in thick membranes [*M. Coleman et al., Nano Research 2015, 8, 1128–1138*].

The lateral dimensions of GO sheets play an important part in controlling microstructures and properties of GO membranes. Either large or small GO sheets have their merits. Usually, the larger the GO sheet sizes, the higher its C/O ratio [*J. Zhao et al., ACS Nano 2010, 4, 5245-5252*], *i.e.,* smaller GO sheets have more oxygenated groups per unit surface area. In fact, the edge-to-area ratio of a GO sheet increases with the decrease of its lateral dimension. However, a larger sheet brings fewer oxygenated groups per unit surface area. Under this condition, larger sheets can absorb less water through hydrogen bonding and lead to a smaller d spacing and improved mechanical properties. The membranes prepared by smaller lateral sizes have shown more and shorter water transport pathways as compared to those prepared with larger GO sheets. The reason is that more gaps exist between the edges of neighboring smaller GO sheets within the membrane. A larger number of gaps provide more passages for molecules and ions diffusing through the membrane in vertical direction to GO sheets. Therefore, this property (lateral sheet size) is useful for building different GO membranes to either maximize the flux through using small sheets or achieve better separation selectivity by means of larger sheets.

3. Challenges and future outlook

GO and rGO membrane filtration processes offer several benefits including flexibility of operation, good mechanical stability, and good removal capability. However, like every other technology, there are some drawbacks that need to be overcome. First, relatively low rejection ability and mechanical stability of GO for selective separation have limited their use in practical applications that require long-term performance stability. Second, although the dissolution of Al^{3+} is an effective way to produce a competent membrane for water filtration, the need for the AAO filter discs currently places size constraints on membranes. Finally, the thickness of membrane significantly regulates the membrane separation performances and controlling the thickness of the membrane is a great challenge. Therefore, GO membranes need additional improvements before commercialization for filtration applications.