Preparation and Application of pressure-driven GO membrane

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Abstract. Membranes occupy essential status in selective separation substances from other liquids or gases. However, development of efficient membrane technology needs to find more new materials with low cost and high efficiency. Graphene oxide (GO), as an attractive two-dimensional material, offers a wide range of opportunities for membrane applications due to unique separation mechanism. In this article, the preparation of pressure-driven GO membrane and its related applications in dye separation, forward osmosis and other fields are introduced. GO membranes are expected to be next generation for precise ionic and molecular sieving which play an important role in vast important fields.

1. Introduction
In recent years, environmental problems have caused great panic in the world and need to be solved urgently [1, 2]. Water treatment technology has many categories, such as in the process of dyes degradation and organic matter removal, which can be completed by catalytic degradation, membrane separation and etc [3-5]. Due to simple operation, low operating cost and high separation efficiency, membrane technology has received more and more attention [6-8]. In the membrane separation process, selection of membrane material is an important part for application. Among advanced materials used for membrane synthesis, metal organic frameworks (MOFs) and graphene oxide (GO) are emerging as two kinds of the best choice. MOFs have large surface area and extraordinary pore structure with clear adsorption affinity, so MOF membranes can hold excellent properties [9]. MOFs can be combined with some natural materials and organic materials to make them relevant. The composites with enough selectivity, hydrophilicity and anti-staining properties have a good application prospect in the future [10, 11]. Since the research on MOF membrane is still in its infancy, its widespread use is subject to certain restrictions. Comparatively, as a famous two-dimensional material, GO has been widely explored and used in different fields of synthetic materials [12-14]. As shown in Figure 1, it can be seen from the structure that on graphene oxide surface a lot of functional groups, such as epoxy, hydroxyl and carboxyl groups, are located at the edge of graphene oxide sheet. Besides, the preparation of graphene oxide and related membranes is more economical and simpler, which can easily realize industrial production and application [15].

When graphene oxide membrane is used for separation, it has a different separation mechanism from the conventional membrane process. As shown in Fig.2, in highly ordered graphene oxide membranes, two adjacent graphene sheets can form a 2D channel that is permeable to water but does not allow unwanted solutes to pass through. Meanwhile, the rich surface of graphene oxide has many
functional groups, which is very beneficial for the target separation. These properties make the multilayer graphene oxide an ideal candidate for molecular sieve membranes [16, 17].

2. GO membrane fabricated by pressure-driven process
According to the publications so far, a majority of GO membranes have been fabricated by pressure-driven process. As shown in Fig.3, GO membranes prepared by filtration to dehydrate the GO suspension by making use of pressure distinction across the membrane. Compared with the membranes made by chemical vapor deposition method which was too complex to be widely used, the prepared membranes by pressure-driven process can be successfully applied in desalination and gas separation. Single GO sheets of very different sizes irreversibly stacked to form double layers when brought together face-to-face, while similar GO sheets were not likely to overlap during monolayer compression because of the edge-to-edge repulsion [18]. The dried membranes produced by vacuum filtration had a layer spacing of about 0.3 nm, and this closely packed GO nanosheet allowed only water vapor arranged in a single layer to pass through the interlayer nanochannel [19].

As shown in Fig. 4, Tang et al. prepared a well-packaged free-standing GO membrane through pressurized ultrafiltration by charging a certain amount of GO aqueous solution into a static battery and filtering through a cyclopore polycarbonate membrane [20]. After filtration, the GO membrane

Figure 1. Structural model of GO.

Figure 2. Separation mechanism diagram of multilayer graphene oxide membrane.

Figure 3. Schematic of GO membrane fabricated by pressure-driven process.
can be dried in the air immediately, and the interaction between the GO nanosheets was promoted by hydrogen bonding interaction, so that the membrane had good stability, mechanical strength and hydrophilicity.

![Diagram of membrane forming system by pressure-driven filtration.](image-url)

**Figure 4.** Membrane forming system by pressure-driven filtration.

Su et al. had fabricated 0.5 to 5µm thick freestanding membranes by vacuum filtration and supported films by rod-coating or spraycoating on the top of polyethylene terephthalate (PET) membranes, metal foils and oxidized silicon wafers [21]. They found chemically reduced GO membranes (especially by HI) exhibited ideal barrier properties to all tested gases and liquids which ensured chemically reduced GO membranes to be used in chemical and corrosion protection that need to isolate of moisture and oxygen. Hong et al. prepared a composite graphene oxide framework film by using pressure-assisted self-assembly filtration technology [22]. The mixed suspension of diamine monomers for crosslinking adjacent GO nanosheets passed through a cellulose acetate substrate at pressure of 5 bar to obtain a diamine-bonded GO composite membrane. Specific interlayer distance must be controlled to realize precise ions and molecular sieving. These composite GO membranes were expected to be used in recovery of organic solvents, seawater desalination, and gas separation [23, 24].

3. Application of pressure-driven GO membrane

### Table 1. GO membranes fabricated by pressure-driven process.

| Graphene-based membrane | Objective | Water flux kg/ (m² h) | Remark | Ref |
|-------------------------|-----------|-----------------------|--------|-----|
| Free-standing GO        | Separating ethanol/water | 3.7 | Pressurized ultrafiltration | [21] |
| rGO/hydroiodic/ascorbic acids | Intercepting all gases and liquids | - | Little structural damage | [22] |
| GO/Diamine Monomers     | Separating ethanol/water | 2.27 | Water concentration: 99.8 wt % | [23] |
| PES/GO                  | Separating humic acid/tannic acid | 2.7 | Capture additional dye molecules | [24] |
| GO/TFNC                 | Pervaporation           | 2.2 | Large porosity 80%           | [25] |

3.1. Retention for organic dyes

Graphene oxide film has good selectivity in Nano filtration and pervaporation. Typical GO membranes were filtrated on variety of substrates by filtration devices which offered certain pressure difference. After partially reduced graphene oxide by refluxing in 0.01 M NaOH aqueous solution for 1 hour, Han et al. prepared a graphene Nano filtration ultra-thin film of about 22-53 nm on a micro porous substrate. The water flux was 21.8 m⁻² h⁻¹ bar⁻¹ and the rejection of dye molecules and salt ions was 99% and 20-60%, respectively [25]. Because they can be bent freely without breaking, they
showed good flexibility. Based on this performance, they can be assembled into more complex membrane modules for widespread use in practical operations [26]. The long-term stability, high performance, low cost and simple preparation process of ultra-thin graphene Nano filtration membrane ensure the big potential in practical and effective water purification.

3.2. Application in forward osmosis.
GO membranes also have latent capacity in forward osmosis. Liu et al. prepared a self-contained ultra-thin reduction GO film by a simple and effective method. GO dispersion was filtered on a mixed cellulose ester filter to formed a supported membrane. The membrane was reduced by hydriodic acid solution and then spontaneously separated from the filter within 1 min when placed on a water surface [27]. Forward osmosis (FO) filtration was applied to demonstrate the permeability and selectivity of the freestanding ultrathin reduced GO membrane whose thickness was 20-200nm. FO filtration demonstrated high permeability and high selectivity of freestanding ultra-thin GO membrane with thickness of 20-200 nm, which was sufficient to overcome the concentration polarization problem inside current membrane, and the GO film was highly repellent to organic and inorganic matters.

3.3. Other Applications
Xu et al. had synthesized graphene oxide-particle composite membranes by vacuum filtration through polycarbonate filter membranes [28]. The progress included preparing stable aqueous dispersion of GO–TiO₂ composite sheets and assembling these composite sheets into aligned stacking membrane by pressure difference. By introducing nanoparticles between the GO sandwich panels, GO membrane with enlarged space and channels were desirably formed and successfully used in separation. Through the rejection and absorption mechanism, the GO-TiO₂ membrane can remove the dye molecules (methyl orange and rhodamine B) in the water when the dead end is filtered, and the removal efficiency can reach more than 90%, indicating the potential application of the membrane in water and wastewater treatment.

4. Conclusion & Outlook
The GO membrane can be simply and effectivley prepared by pressure-driven process, in which the cost is low and the operation is easy. Therefore, the GO membrane has a very important value for industrial application. At the same time, the layered GO membrane with the spacing between GO layers as the transport channel is expected to be the next generation of high-quality separation membrane with high selectivity, high throughput and pollution resistance. In the context of the gradual deterioration of the environment, two-dimensional materials represented by graphene have great prospects in the field of membrane separation, and will inevitably play a more important role in continuous innovation.

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