Two-dimensional Layer-by-layer Assembled Graphene Oxide Membranes in Water Treatment

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Abstract. Graphene oxide membranes (GOMs) are ultra-thin, high-throughput and energy-efficient membranes for precise ion and molecular sieving in aqueous solutions. The spacing control of the graphene layer has a great influence on the separation effect of the material, and is of great significance for achieving the balance between the separation degree and the flux. Due to the particularity of the graphene oxide structure, the layer spacing can be precisely manipulated when the multi-layers are self-assembled. Layer-by-layer self-assembly is an important method for preparing graphene oxide membranes. Based on the unique structure and properties of graphene oxide membranes, layer-by-layer self-assembly method and its application is reviewed in this paper.

1. Introduction
Increasing environmental pollution has caused serious hazards to our residents. Under the current environmental governance strategy, researchers begin to improve traditional techniques to achieve simple, rapid and efficient processes. For example, photocatalytic degradation[1,2], MBR reactor[3] and other membrane combination processes[4]. Meanwhile, they are also actively looking for and developing new materials for pollution treatment. These new materials can combine with membrane producing to achieve better performance[5]. Metal organic frameworks (MOFs) and graphene oxide are among the best in these new materials, and have received wide attention around the world in recent years. The natural structure of MOFs has more advantage than many materials. It can be combined with some natural materials to make microcapsules[6], and can also be applied in the field of membrane science[7,8]. Similarly, graphene oxide (GO) can also be shaped into capsules, microspheres and etc[9,10], which is more widely used in the field of separation[11]. Compared with MOFs, when graphene oxide is applied to membrane separation, the surface of GO contains a large number of functional groups, which can accurately screen the target ions and have good mechanical properties. Therefore, the unique two-dimensional structure of graphene oxide and good water stability make graphene oxide an ideal candidate material for membranes, which can be removed by the action of external force, such as pressure difference or electrostatic attraction[12]. Meanwhile, the graphene oxide...
membrane has special physicochemical properties, and has a good prospect of excellent selective screening ability and much higher throughput than that of conventional industrial nanofiltration membranes[13-14].

2. Structure and Property of Graphene Oxide Membrane
As shown in Fig. 1, graphene oxide has a very large specific surface area. Its surface contains a wide variety of functional group distributions, which makes the graphene oxide nanosheets negatively charged[15,16]. The functional groups on GO nanosheets offer important chemical reaction binding sites for chemical grafting or modifying reaction to facilitate the interaction of GO sheets with different kinds of organic and inorganic materials and promote the use in different areas [17,18].

![Fig. 1. Structural model of GO.]

GO membranes possessing stacked stratified structure are shown in Fig. 2. The interlayer distance of the lamellar graphene membrane is about 0.335 nm. This value increases to 0.82nm for GO membrane with the presence of functional groups and adsorption of liquid molecules in the interlayer. Joshi et al. reported that ions or molecules whose hydrated radii was smaller than the GO nanochannel can permeate through the GO membrane unimpeded at a speed of many orders of magnitude faster than the diffusion mechanism while larger ions or molecules are blocked. This phenomenon can be explained by interlayered space dominant sieving mechanism[19,20].

3. GO membrane fabricated by layer-by-layer assemble
To solve the critical problem of GO membranes’ re-dispersing in aqueous solution, as illustrated in Fig. 3, adjacent GO nanosheets must be integrated together through a sort of force linking both the substrate and outermost layer tightly[21]. Covalent crosslinking bonding technique is to establish covalent bonding between abundant oxygenic functional groups on GO nanosheets and appropriate crosslinking agent molecules by relevant chemical reaction. Electrostatic adhesion technique is to attract negatively charged GO nanosheets by substrates or polyelectrolytes with positively charge. Of course, in addition to electrostatic attraction, van der Waals forces, hydrogen bonding and hydrophobic interactions also act to some extent[22].
As Goh et al. reported, GO dispersion in certain concentration was filtered through substrate filter, and then peeled off or kept intact and dried. Several layered GO membranes were made by spin-coating or dip-coating GO nanosheets on microporous polymer membranes[23]. In fig. 4, method one is a kind of dip-coating method which is to immerse the substrates in GO solution. Researchers withdrew and removed containing water by a spin coater or heating under a little higher temperature. Method two is a typical drop spin-coating method which is to place the substrates on a spin coater with GO solution dropping down at the same dropping velocity on the centre of the spinning substrate.

**Fig. 3.** Preparation of graphene oxide film by layer-by-layer self-assembly.

**Fig. 4.** Two different GO LBL coating methods.

### 4. Application of Graphene Oxide Membranes

Hu et al. cross-linked 1,3,5-benzenetricarbonyltrichloride and graphene oxide nanosheets on a polydopamine-coated polysulfone support, and prepared different thick membranes by depositing different amounts of GO nanosheets layer by layer[21]. The cross-linking tuned charges, functional groups and spacing of the GO nanosheets and enhanced interlayer force to ensure the membranes’ stability. Goh et al. prepared a statically fixed GO membrane by crosslinking a negatively charged graphene oxide nanosheet on a PEI hollow fiber membrane substrate prepared by phase inversion[24]. Due to the small pore size of membrane surface, the narrow pore size distribution and the low hydrodynamic resistance between the nanosheet layers, the membrane can achieve high water permeability without affecting membrane selectivity.

Yeh et al. put laminated GO nanosheets onto thin-film nanofibrous composite membranes by spin coating and fabricated multilayered pervaporation membranes for ethanol dehydration[25]. With a total
thickness of 93 to 618 nm, the GO barrier layer on the support surface formed by self-assembly of GO sheets performing much better properties than common commercial polymeric membranes. These membranes owned larger water flux but lower separation factor compared to membranes fabricated by vacuum filtration which were restricted to be used in particular territory. Chen et al. prepared a graphene oxide and nylon 6 composite membrane by a layer-by-layer self-assembly process using a combination process of electrospinning and electrospray. This method can rapidly prepare a graphene oxide film with a large area. At the same time, due to the tight locking structure of the nylon 6 nanofiber network, the membrane had good mechanical stability[26]. Under the action of polydimethyl diallyl ammonium chloride, Liu et al. also produced a sandwich composite membrane by layer-by-layer self-assembly technology of graphene oxide and oxidized carbon nanotubes, which had good stability and high flux[27].

Table 1. Application of Layer-by-layer Assembled Graphene Oxide Membranes

| Supporting membrane | Cross-linking | Preparation method | Permeability | Ref |
|---------------------|--------------|--------------------|--------------|-----|
| Polydopa-coated PS  | 1,3,5-benzene| Layer-by-layer deposition | 8.00-27.6LMH, 93% | [21] |
| PAI–PEI hollow fiber| PEI/ GO      | Dip-coating        | 25.0LMH, 86% | [24] |
| TFNC GO/ TFNC       | GO/ TFNC    | Spin coating       | 2.2LMH, 68%  | [25] |
| Nylon 6             | GO@nylon 6  | Electrospraying/ electrospraying | 11.15LMH, 95% | [26] |
| PAN substrate       | PDDA/ GO/ OCNTs | Layer-by-layer deposition | 28.53LMH, 94.2% | [27] |

5. Conclusion & Outlook
GO membranes for water treatment applications have made great progresses in recent years. Freestanding and supportive GO membranes have demonstrated that they can be engineered to exhibit the desired water treatment behaviors. In the past two decades, layer-by-layer self-assembly techniques have been widely used in the preparation of graphene oxide membranes with various functions. Polymers and nanoparticles can be alternately deposited on a substrate by electrostatic attraction of opposite charges or hydrogen bonds, which is easy to be operated[28]. By adjusting the concentration of GO in the suspension, as well as the temperature and PH of the reaction, the thickness, transparency and permeability of the GO membranes can be precisely controlled. All these will bring unlimited possibilities for the development of novel graphene oxide membranes.

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7. References
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