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RESEARCH ADVANCEMENTS IN THE IDENTIFICATION OF TRANSMISSION ROUTES AND STRUCTURAL ALTERATION TECHNIQUES FOR GRAPHENE OXIDE MEMBRANES

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Abstract: This article explains the transmission and separation and interception mechanisms of graphene oxide films, and based on this, it is concluded that the interlayer spacing can be controlled through reduction, cross-linking, cation control, intercalation, physical restrictions, etc. Chemical physical methods; and internal structural defect control mainly through creating nanopores and sealing defects. Therefore, summarizing and analyzing the application limitations of graphene oxide and proposing modification methods and measures for graphene oxide membrane materials can lay a good foundation for the practical application of graphene oxide membranes.
Keywords: Graphene oxide film; Separation mechanism; Transmission channel control; Structural defects; Layer spacing

1 INTRODUCTION

Graphene has a 2D structure in a honeycomb shape, with a single layer of carbon atoms regularly arranged in a hexagonal lattice, with a thickness of only about 1 nanometer. The dense delocalized cloud formed by its π-orbitals blocks the distance between the aromatic rings of graphene, making it difficult for any molecule to pass through the monolayer structure, including the smallest helium. Graphene oxide (GO), as one of the main derivatives of graphene, still retains the original properties of graphene such as large specific surface area and strong mechanical properties. In addition, GO contains abundant oxygen-containing functional groups such as hydroxyl, carboxyl, carbonyl, and epoxy groups within the plane and at the edges. By modifying the above oxygen-containing functional groups, the physical and chemical properties of GO can be further improved for the following reasons:
Hydrophilic functional groups can contribute to the stable dispersion of GO in aqueous solution and ensure the orderly stacking of GO nanosheets; secondly, the oxygen-containing functional groups on GO can be prepared by controlling its microstructure and physical and chemical properties through graft modification and other means. To form a GO-based hybrid membrane, the oxygen-containing functional groups on GO can also react with water molecules, CO2, etc. through hydrogen bonds and charge interactions, thereby improving the permeability efficiency of the GO membrane; in addition, the oxygen-containing functional groups on GO can make GO 2D nanochannels of 0.7~1 nm are maintained between the layers. This nanochannel can promote the effective passage of small molecules through the GO membrane. In view of the above-mentioned mode of action, characteristics and application possibilities of GO membrane, the preparation of GO into membrane separation materials has gradually attracted widespread attention from scientific researchers.

2 GRAPHENE OXIDE FILM TRANSMISSION AND INTERCEPTION MECHANISM

For laminar flow GO membranes, there are currently two main molecular transmission channels: interlayer nanochannels formed by adjacent nanosheets and GO membrane pores and structural defects. During the mass transfer process of the GO membrane, molecules first enter the pore channels and structural defects of the GO membrane, and then pass through the channels between the membrane layers. At the same time, since the GO membrane is a graphene-derived material, in addition to the interlayer channels and pores or defects in the graphene layer, the abundant functional groups on the GO membrane also play a certain role in determining the molecular transport of the graphene membrane.

2.1 Channels between Membrane Layers

Since when water molecules pass through a dense graphene film, there is a capillary driving force and low friction flow between the two-dimensional interlayer channels of the graphene sheets, so in order to evaluate the flow characteristics of these water molecules between the nanolayer channels, Geim [1] used Poiseuille's law to describe the molecular flow in the layered graphene oxide structure. The formula is as follows:

$$J = \frac{d^4 \cdot \Delta P}{RL^2 \ \eta h} \quad (1)$$

Among them: d: the effective vertical distance between adjacent graphene oxide layers; L: the average lateral length of graphene oxide; eta: the viscosity of water; h: the thickness of the graphene oxide film.

2.2 Membrane Pores and Structural Defects

In addition to interlayer channels, structural defects and pore channels on the graphene sheet structure can also be effectively used to selectively transport small molecules. These defects and pores can provide easy and rapid flow of small molecules through the graphene oxide layer. Channels, that is, structural defects in graphite sheets, reduce L (the average length of nanosheets), which can increase the flux according to formula (1).
In addition, another function of defects and pores is that through careful stacking of graphene, it can have the property of intercepting molecules [2-3]. Generally speaking, the flow of a gas phase mixture passing through a graphene oxide membrane can be explained by the Knudsen theory, and its theoretical formula is as follows (2).

$$J = \frac{\Delta P}{\sqrt{2\pi m K_B T}} \quad (2)$$

Among them, J is the gas permeability; P is the pressure; m is the molecular mass; KB is Boltzmann's constant; T is the reaction temperature.
To sum up, molecules mainly pass through the graphene oxide-based membrane through synergistic effects, that is, interlayer channels, structural defects, pores and functional groups. Based on the above-mentioned membrane transport mechanism and pollutant interception mechanism, we can start by regulating the transmission channels between membrane layers, introducing functional group modifications, and regulating GO membrane defects, in order to improve the transmission and separation efficiency of the GO membrane and achieve the interception and separation of pollutants.

3 METHODS TO IMPROVE THE TRANSMISSION AND SEPARATION EFFICIENCY OF GO MEMBRANE

Controlling the transport channels of membranes is critical for the rapid transport and separation of molecules. The interlayer spacing of GO membranes has a significant impact on the molecular transport efficiency and can be tuned through chemical and physical methods. In addition to the interlayer spacing, defects and pores in GO membranes can provide transport pathways for improved transport properties. In view of different target pollutants and pollutant disposal objectives, this article mainly summarizes the chemical and physical methods to improve membrane transmission channels and regulate the internal pores and structural defects of GO membranes, and summarizes the methods to improve the efficiency of GO membrane transmission and separation membranes. The specific contents are as follows.

3.1 Chemical Control of Interlayer Structure

When the GO membrane separates liquid media, due to the capillary action of the liquid and the solution, the GO membrane expands due to the capillary force, causing the interlayer spacing of the GO layered membrane to become larger, and the separation ability of the membrane gradually becomes worse, and in severe cases, it may even cause Leading to the dissociation of GO layered membrane [4]. Therefore, controlling the interlayer spacing of GO layered films is of great significance for controlling the transport pathway of GO and improving the stability of GO films. Several commonly used chemical methods to control the spacing of GO nanosheets are listed below: 1. Reduction; 2. Cross-linking; 3. Cation control.

3.1.1 Reduction method

Since GO layered membranes with smaller interlayer spacing are more conducive to screening small molecules, how to reduce the interlayer spacing of GO membranes has become a research hotspot. Currently, one of the most commonly used methods to reduce the interlayer nanochannels of GO membranes is the reduction method. Currently known reduction methods mainly include chemical reduction and heat treatment [5-7].
Chemical reduction method is one of the common methods to regulate the spacing between GO film layers. It mainly achieves the purpose of regulation by reducing the oxygen-containing functional groups in the GO film and reducing the interlayer spacing of the GO film. After comparing the reduction mechanism, Guo Jianqiang et al. [5] pointed out that the core of reduced graphene oxide is the reduction of hydroxyl groups and the formation process of new C=C double bonds. As shown in Figure 1, free-standing ultrathin rGO films with thicknesses as low as 20 nm were prepared through hydroiodic acid (HI) vapor and water-assisted layered reduction of GO films [8]. The reduction of hydrogen iodide can remove some of the oxygen-containing functional groups on the surface of the GO film, thereby reducing the interlayer spacing of the original GO film from 8.7 Å to 3.5 Å of the rGO film. The reduction of the interlayer spacing makes the GO membrane more conducive to screening small molecules.

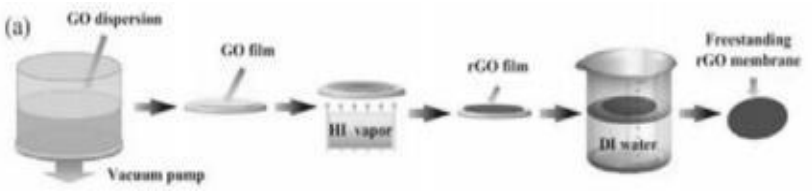

Figure 1 Schematic diagram of the process of preparing free-standing rGO membranes through hydrogen iodide vapor reduction method [8]

Although the size of the nanochannels of the GO membrane can be changed using chemical reduction methods, if the chemical reagent used is strong acid vapor, it will cause damage to the environment. In contrast, heat treatment can reduce the interlayer spacing more gently.

Kim et al. [6] prepared GO membranes with different oxygen-containing functional groups through heat treatment. The study found that heat treatment operations at different temperatures will affect the content of oxygen-containing functional groups in the GO film, thereby changing the interlayer spacing structure. When studying the effects of oxygen-containing functional groups and interlayer spacing on the penetration of ions and water, when the temperature increased from 175 ℃ to 220 ℃, the content of oxygen-containing functional groups on the GO surface gradually decreased, and the interlayer spacing increased from 8.0 of the original GO membrane. Å decreases to 5.0 Å at 220 °C. This shows that within a certain temperature range, the higher the temperature during heat treatment, the lower the content of oxygen-containing functional groups.

The above studies show that chemical reduction and heat treatment are effective ways to partially reduce GO membranes. After the oxygen-containing functional groups on the GO membrane are partially oxidized, the interaction between the membrane layers is reduced. When the external conditions remain unchanged, the interlayer spacing will be reduced accordingly, thereby improving its screening ability.

3.1.2 Cross-linking method

Appropriate reduction can effectively improve the screening ability of GO membranes, but when the degree of reduction is too high, most of the oxygen-containing functional groups will be eliminated, and the interaction between the sheets will be too strong, leading to the collapse of the nanopores. Another method of modifying GO membranes is the chemical cross-linking method, which usually inserts specific small molecules or polymers that can react with oxygen-containing functional groups to achieve the preparation of composite cross-linked GO membranes. Research has found that a large number of nanomaterials and molecules are used to insert between graphene oxide layers to form a hybrid material, and then increase the molecular flow rate by increasing the interlayer spacing, increasing the pure water flux several times [9-11].

Zhang Yongzhi et al. [12] used polar small molecules urea (UR) and ethylenediamine (EDA) as cross-linking agents to prepare GO/CA, GO-UR/CA and GO-EDA/CA membranes respectively, and measured Water flux and rejection efficiency of three membranes. The results show that GO-UR/CA has the best ion interception effect and can effectively strengthen the strength of the GO membrane. At the same time, there is not much difference in water flux between the three. This is due to the presence of monomeric carbonamides on GO-UR/CA. The molecular weight of carbonamide itself is not large, and there is a carbonyl group on it, so it can limit the change of layer spacing more efficiently.

In addition, relevant research shows that composite graphene oxide framework (GOF) membranes can be prepared by cross-linking ethylenediamine (EDA), butylenediamine (BDA) or p-phenylenediamine (PPD) through pressure-assisted self-assembly device technology filtration [13]. The interlayer spacing of the unmodified GO film changes greatly from the dry state to the wet state, while the interlayer spacing of the GOF film cross-linked by EDA, BDA and PPD changes very little from the dry state to the wet state. This is because for the GO film, the hydrogen bonds and π-π interactions are destroyed, causing the interlayer spacing to be stretched. For GOF films, the covalent bonds between carbon and nitrogen well resist the stretching phenomenon of the interlayer spacing.

The composite membrane prepared by inserting various small molecules or polymers that can react with oxygen-containing functional groups into the GO membrane has greater improvements in hydrophilicity, desalination, etc. than the original one. The GO produced by this cross-linking method Membranes have great application value in the industrial field.

3.1.3 Cation control

The cation control method based on cation-π interaction can fully adjust the interlayer spacing, so that the GO membrane can meet the requirements for screening small molecules, and this method can effectively suppress the tendency of the GO membrane to expand when separating liquids, thereby strengthening the GO membrane. stability.

Park[14] et al. prepared alkali metal ion-modified GO membranes by vacuum filtration of GO solutions added with MgCl2 and CaCl2 to study the effects of Mg2+ and Ca2+ on GO membranes. The results showed that the mechanical strength of the membrane was significantly improved. This is because the cation-π interaction generated between cations and oxygen strengthens the force between graphene oxide sheets, thereby improving the stability of the GO film.

In addition to monovalent and divalent cations, trivalent cations can also be used to control the interlayer distance of GO membranes. Liu [15] et al. used two trivalent cations (Al3+ and Fe3+) as cross-linking agents to assemble GO nanosheets on PVDF carriers. The study found that Al3+ and Fe3+ can greatly enhance the bonding strength between GO nanosheets through electrostatic interactions and coordination bonds, thereby improving the stability of the GO film.

3.2 Physical Methods Control Interlayer Structure

Chemical methods perform well in controlling interlayer transport pathways, but they also have some shortcomings. GO nanosheet molecules/cations have an inherent geometric structure, and it is difficult to form interlayer channels that are small enough and hard enough through chemical methods alone to achieve efficient separation of multiple media in the pressure-driven separation process. In addition to chemical methods, physical methods also have good feasibility, which

can inhibit the out-of-plane expansion of graphene oxide laminates and adjust the interlayer spacing, thereby accelerating water permeability and high interception rates of various salts [16]. The following methods all use physical methods to fine-tune the transmission pathways of layered graphene oxide films, which can be divided into two categories: physical intercalation and physical confinement.

3.2.1 Physical intercalation

Physical intercalation mainly prepares GO hybrid membranes with efficient separation performance by inserting materials with various sizes into adjacent nanolayers of GO. The interlayer spacing of graphene oxide nanosheets can be precisely controlled through physical intercalation, and the rapid selectivity of graphene oxide films to water and ions can also be improved.

Research has found that combining inorganic nanomaterials with graphene oxide can produce high-selectivity and high-flux GO membranes [17]. Halloysite nanotubes (HNTs) are one-dimensional natural hollow tubular nanomaterials. HNTs have few tube-tube interactions and can be evenly dispersed on the membrane surface. They have a large surface area and the inner surface is positively charged. Other advantages also make it an ideal inorganic intercalated nanomaterial. Polydopamine (PDA) is a pigment that exists in nature and is biocompatible and degradable. It also has good conductivity, hydrophilicity, adhesion and redox activity [18]. Adding PDA to the composite membrane can improve the stability of the composite material. Therefore, PDA and HNTs can be assembled on the surface of cellulose acetate membrane (CA) to synthesize a reduced (PDA/RGO/HNTs) membrane (Figure 2) [19]. Experiments show that the flux of the PDA/RGO/HNT membrane has been significantly improved, and the rejection rates of methylene blue (MB), Congo red (CR), Cu2+, and Cr3+ are 99.72%, 99.09%, 99.74%, and 99.01% respectively. The circulation and antifouling test results show that the HNTs modified membrane exhibits superior antifouling ability.

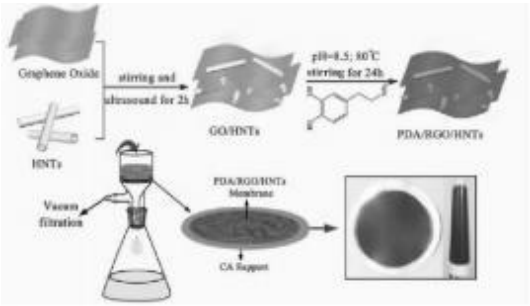

Figure 2 Preparation method of PDA/RGO/HNTs membrane [19]

The above research shows that the physical intercalation method has an excellent effect in improving the anti-fouling ability and dye interception ability of GO membranes. At the same time, materials such as HNTs can effectively control the layer spacing after being inserted through the physical intercalation method, thereby increasing the water separation flux.

3.2.2 Physical limitations

Although physical intercalation has good effects on anti-fouling ability and dye interception ability, its method is relatively simple and has many requirements on the inserted materials, so it remains to be studied. Different from the simple physical intercalation method, physical confinement is a method that uses external force or pressure to limit the spacing of the graphene oxide membrane, thereby improving the separation ability of the graphene oxide membrane. Physical constraints can effectively suppress the out-of-plane expansion of graphene oxide laminates and control the interlayer spacing, thus greatly improving the repellency of the graphene oxide membrane to various salts to achieve the purpose of improving interception efficiency and flux.

Abraham et al. [20] used epoxy resin to encapsulate multi-layer graphene oxide laminates to prepare physically constrained graphene oxide films (Figure 3). Unlike isotropic materials with omnidirectional swelling behavior, the anisotropic GO film with a two-dimensional structure swells almost only in the vertical direction, thereby forming a large interlayer spacing in water. Therefore, external force or pressure in the vertical direction can effectively limit the expansion of the GO membrane, thereby improving the sieving ability of the GO membrane.

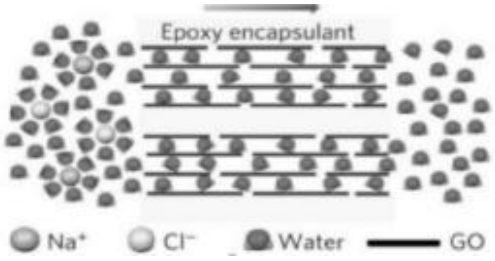

Figure 3 Schematic diagram of ion/water penetration of epoxy resin encapsulated graphene oxide laminate[20]

Wei [21] et al. found that under higher feed pressure, due to the narrow transport channel, the Na2SO4 removal rate of the compacted graphene oxide membrane can be increased from 21.3% to 85.8%.

The physical confinement method can better adjust the interlayer spacing of the GO film and prepare high-performance GO film. Adjusting the distance between GO membrane layers through external pressure has the advantages of simplicity and speed, which makes it better applicable to the field of industrial separation.

3.3 Internal Defects/Pores/Edge Control

For GO membranes, the interlayer nanochannels of adjacent nanosheets and the inherent defects/pores/edges of GO nanosheets are critical to the mass transport of the membrane. There are currently two main ways to adjust the inherent defects/pores/edges of GO membranes: one is to create nanopores to achieve more precise and faster separation; the other is to seal the defects/pores/edges to achieve high selectivity and high rejection.

3.3.1 Creating nanopores

In recent years, atomically thick porous graphene has received increasing attention in separation applications due to its unique porous structure combined with the inherent properties of graphene. At present, the preparation of porous GO membranes mainly includes etching, thermal reduction, etc.

The etching method mainly uses high-energy electron beams, catalysts, etc. to remove carbon atoms at specific locations to create pores. Lin[22] and others deposited silver on the surface of graphene through thermal decomposition of silver nitrate and heat treated it. After removing the excess silver, pores with a diameter of five to tens of nanometers were produced on the graphene surface (Figure 4). Although this method is relatively simple to operate, the structure of the nanopores produced cannot be controlled. Another more effective way to create it is thermal reduction.

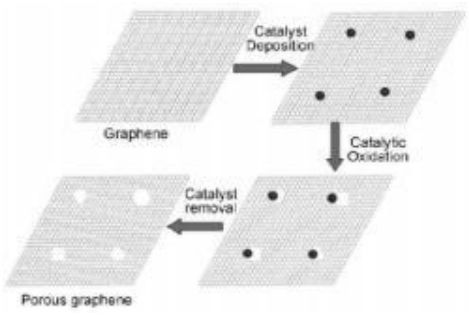

Figure 4 Catalytic oxidation etching of graphene [22]

The thermal reduction method uses carbon as a reducing agent to reduce metal oxides to obtain metal elements, and the carbon atoms themselves are etched during the reduction process [23]. Peng [24] et al. found that when GO is subjected to high-temperature and rapid thermal reduction treatment, it can release huge gas pressure between layers, thereby effectively punching holes in the GO sheets. As the heating rate increases, the pores The increase in number density improves the transmission efficiency and pure water flux of the GO membrane.

Etching and thermal reduction methods can effectively create nanopores on GO to prepare porous graphene, allowing for more precise and rapid separation. Porous graphene has high application value in the field of separation and has become the focus of researchers.

3.3.2 Seal defects/voids/edges

In addition to creating nanopores and defects, sealing or plugging of defects/pores/edges in GO membranes has also been shown to improve GO membrane screening capabilities. O'Hern et al. [25] prepared nanoscale porous single-layer graphene with excellent screening performance through a multi-step defect sealing process. Using atomic layer deposition to selectively fill nano-defects in graphene, and then using interfacial polymerization of nylon 6,6 to seal large cracks (Figure 5), a centimeter-scale single-layer graphene film with significantly low leakage was obtained For unsealed single-layer graphene membranes. After the hole sealing treatment, nanopores were introduced into the single-layer graphene through high-energy gallium ion bombardment and acidic potassium permanganate chemical etching. The prepared nanoporous graphene membrane has a rejection rate of 70% for MgSO4.

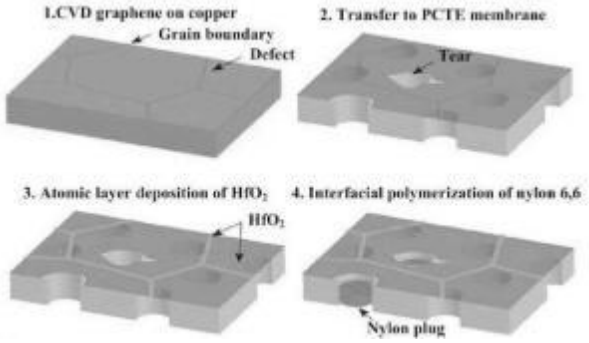

Figure 5 Schematic diagram of graphene film preparation and defect sealing procedures [25]

In summary, GO membranes with high retention properties can be prepared by selectively sealing or blocking the inherent defects/pores/edges in the GO membrane. Currently, this method has gradually become the focus of scientific researchers.

4 CONCLUSION

Membrane separation technology has the advantages of high separation efficiency, easy operation, simple equipment, no phase change, and energy saving. It has very broad application prospects in the fields of water treatment, materials and chemical industry [26]. Compared with graphene, GO has more oxygen-containing functional groups and has a monolayer structure. Therefore, GO has better thermal conductivity, electrical conductivity and mechanical properties. Based on the above advantages, GO is also used as a composite membrane material for wastewater treatment, desalination, gas separation, etc.

Based on the separation mechanism of GO membrane materials, this article summarizes that the controlling factors of GO membrane materials are mainly to adjust the graphene layer spacing and improve its own structural defects and pore composition. It also introduces the use of chemical and physical methods to regulate the layer spacing, create or seal nanopores, etc. Contents to prepare the current status of GO composite membranes with good stability and high separation efficiency. At present, GO membranes do not have the capability of large-scale production after preparation and modification. Therefore, further research on the functionalization of GO membranes is needed to better lay the foundation for the practical application of GO membrane materials.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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