ISSN: 2414-1895 DOI: 10.6919/ICJE.202205_8(5).0107

Research Progress of Graphene Oxide Composite Membrane

Yonghao Chen[1], Huiying Li[1], and Xinyu Zhao[2]

[1] School of Pharmacy, North China University of Science and Technology, Tangshan 063210, China

[2] School of Mechanical Engineering, North China University of Science and Technology, Tangshan 063210, China

Abstract

As a novel two-dimensional material with excellent physical and chemical properties, graphene oxide (GO) has attracted great attention in the field of membrane science. In this paper, the common preparation methods of GO membrane, such as vacuum filtration method and spin coating method, are introduced based on membrane technology and GO characteristics. At the same time, based on its membrane-forming characteristics, the modification schemes corresponding to the problems were combed. Finally, the application and development of GO membrane were summarized and prospected on the basis of previous research practice.

Keywords

Graphene Oxide; Membrane Science; Preparation and Modification; Composites.

1. Introduction

Membrane exist widely in nature, especially in life activities. Broadly, a membrane is a material that can separate the interface between two phases and has a selective permeability barrier [1]. Membrane products play an irreplaceable role in modern life. Nowadays, membrane technology is mainly used in separation, purification and energy conversion, among which typical products are reverse osmosis membrane (RO) for seawater desalination and household water purifier, membrane bioreactor (MBR) for municipal sewage treatment, etc.

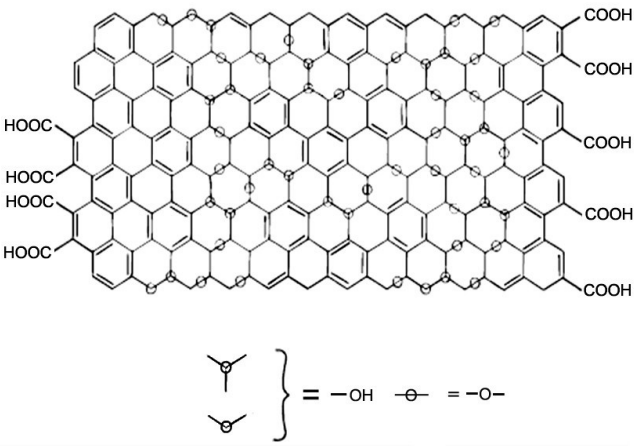

Fig. 1 Structure of graphene oxide [2]

ISSN: 2414-1895 DOI: 10.6919/ICJE.202205_8(5).0107

At the beginning of the 20th century, graphene was prepared by two professors from Manchester University in England by micromechanical stripping, which is a two-dimensional carbon nano-material containing sp2 hybrid carbon atoms and showing hexagonal honeycomb properties. Because of the difficulty in preparing monolayer graphene, people pay attention to its derivative GO [3]. Compared with graphene, GO has the advantages of low production cost and easy processing. In recent years, great progress has been made in the research of GO, which can realize GO functionalization. Because of its porous structure, anti-fouling and strong hydrophilicity, GO is very suitable as a high-efficiency membrane separation material. The layer spacing, groups and chemical stability of GO can be controlled by special preparation and modification methods to meet the requirements of separation and purification, and it is also a new material with great application prospect. In this paper, the common preparation and modification methods of GO composite membrane prospected and considered according to the current problems and pain points.

2. Preparation of Graphene Oxide Membrane

At present, scholars have developed and used a variety of membrane preparation methods including vacuum filtration, spin coating, layer-by-layer self-assembly and volatilization-induced self-assembly. The vacuum filtration method is the most common and simple method to prepare GO membrane.

2.1 Vacuum Suction Filtration Method

In the vacuum suction method, GO in uniformly dispersed GO suspension and other components of the composite membrane are stacked on the basement membrane below by van der Waals force through a vacuum suction pump [4], and the GO composite membrane is obtained after the composite membrane is completely dried and subsequently treated. The thickness of the membrane depends on the GO content in the concentration of the membrane solution, and the size of the membrane depends on the sizes of the filter and the basement membrane.

2.2 Layer-by-layer Self-assembly Method.

This method is a classical method developed by Decher and other scholars to prepare ultra-thin membrane materials based on intermolecular interaction [5]. Because of the functional groups such as carbonyl and carboxyl groups on the surface of GO, it is negatively charged in solution. As the building unit of layer-by-layer assembly, it can be regarded as a two-dimensional polymer anion, which can be constructed into a highly ordered and controllable layered membrane material together with positively charged substances. This method is widely used, and the membrane structure is highly controllable, but the time cost is also high.

2.3 Spin Coating

Spin coating method refers to adjusting the temperature and rotation speed of the substrate under heating, and coating GO dispersed droplets on the substrate to form a uniform and flat GO diaphragm. Because the membrane is prepared under heating condition, the water molecules between GO lamellae are easily removed, and a compact membrane structure with small interlayer spacing is formed. However, this method needs to control many factors including rotation speed, temperature and so on.

3. Modification of Graphene Oxide Composite Membrane

In order to have better physical and chemical properties of membrane, researchers often achieve this goal by modifying membrane. In recent years, the modification of GO membrane has become one of the research hotspots in this field [6], and the main directions focus on surface modification and material modification.

3.1 Surface Modification

Due to the deprotonation of oxygen-containing groups on the surface of GO in aqueous solution, the GO membrane is usually negatively charged, which is not conducive to its stability in solution.

ISSN: 2414-1895 DOI: 10.6919/ICJE.202205_8(5).0107

Usually, the separation characteristics of membrane are improved by introducing corresponding functional groups. Common modification techniques include polymer grafting, plasma treatment, chemical reaction modification and so on. Polymer grafting method is the most effective method mentioned above.

3.2 Post-processing

It has been found that heat treatment of the composite membrane at a certain temperature can change the size of the pore in the membrane. At high temperature, the pore shrinks, the surface is more compact, and the rejection rate will be relatively improved. Some chemical reactions can also change the surface and pore structure of the membrane, thus regulating the performance of the composite membrane.

3.3 Material Modification

The material modification of membrane is mainly through blending, crosslinking and addition. Adding crosslinking agent to form network structure can effectively improve the stability of membrane. Adding additives into the casting solution can affect the microstructure of the membrane, thus changing the mechanical strength and separation performance of the membrane.

4. Application of GO Membrane

The excellent physical and chemical properties of GO have caused the research heat of graphene materials. According to its advantages, it can be applied in different fields after different treatment means. Especially in the application of membrane making, the unique two-dimensional structure of GO membrane has high water flux and selective permeability, which effectively enhances the water treatment effect.

4.1 Removal and Recovery of Heavy Metal Ions

Metallurgical and other industrial wastewater contains a large number of heavy metals such as copper, mercury, lead and so on, which do great harm to human health and ecological environment. At present, the removal of heavy metal ions from industrial wastewater by GO adsorption membrane with abundant oxygen-containing functional groups has made preliminary progress. Li et al. prepared GO membrane and verified its adsorption capacity for heavy metals in water. The experimental results show that the maximum adsorption capacity for Cd2+ and Co2+ is 106.3 mg g-1 and 68.2 mg g-1 respectively [7].

4.2 Oil-water Separation

GO is considered to be an ideal material for separating oil-water mixture because of its rich carboxyl, carbonyl and other oxygen-containing functional groups on its surface, which makes it easily soluble in water to form dispersion. In the process of oil-water treatment, the surface defects and nano-lamellar gaps of GO membrane can achieve the effect of oil-water separation by providing water molecule transport channels; Its hydrophilic property can prevent oil droplets from gathering on the membrane surface, thus enhancing the pollution resistance of the membrane.

4.3 Gas Separation

Because there are nano-scale two-dimensional selective channels between GO layers and selective nano-defects on the surface, molecules smaller than the size of nano-channels and defects can pass freely, so GO membrane can also be used for selective separation and purification of gases. In the application of multilayer GO membrane, gas is mainly transferred in the channel, and the selective separation of different gases can be realized by adjusting and controlling the channel by different preparation and modification methods.

5. Conclusion

At present, most researchers focus on the separation performance of GO membrane, such as surface modification, layer spacing control and so on, in order to obtain membrane materials with good

ISSN: 2414-1895 DOI: 10.6919/ICJE.202205_8(5).0107

separation performance and high throughput. Due to the problem of mass production of graphene and GO, how to reduce the membrane production cost still needs further study. In addition, the large-scale production of GO membrane, the identification and treatment of membrane fouling, and the utilization of waste membrane s are still issues worthy of deep consideration and discussion by researchers.

Acknowledgments

Innovation and Entrepreneurship Training Program for College Students of North China University of Science and Technology, China.

References

[1] Wang Z, Wang Z, Gao X L et al. Fundamentals of film separation technology [M].Beijing: Chemical Industry Press, 2019.01.

[2] Yang Y G, Chen C M, Wen Y F, Yang Q H, Wang M Z. Graphene oxide and its composite with polymer [J]. New Carbon Materials, 2008, (03): 193-200.

[3] Wang Y, Li S, Yang H, et al. Progress in the functional modification of graphene/graphene oxide: A review[J]. RSC Advances, 2020, 10(26):15328-15345.

[4] Li W Q, Chen W G, Cui X J, et al. Research progress on preparation, modification and application of graphene oxide films [J]. Surface Technology, 2021, 50 (2): 12.

[5] DECHER G. Fuzzy nano assemblies: Toward layered polymeric multicomposites [J]. Science, 1997, 277(5330): 1232-1237.

[6] Tian L, Liu T, Sun K N. Research progress of graphene oxide film for water purification [J]. Acta Chemical Engineering Sinica, 2020, 71 (9): 19.

[7] ZHAO G, LI J, REN X, et al. Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion poll-ution management[J]. Environmental science & technology, 2011, 45(24): 10454-10462.