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Graphene Oxide Composite Membranes in Oil-Water Separation: A Review

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Abstract: The advantages of graphene oxide composite membranes in the field of oil-water separation are introduced. The potential application status of various graphene oxide composite membranes, such as ethylenediamine cross-linked graphene oxide membranes and ceramic-based graphene membranes, for oil-water separation is reviewed. The preparation processes and test results of several graphene oxide composite membranes are described and summarized. The effectiveness of these membranes in oil-water separation is analyzed, and the performance of several products is compared. This paper aims to provide readers with a quick understanding of the oil-water separation performance of several graphene oxide composite membranes, thereby facilitating their research.

Keywords: Graphene oxide; Oil-water separation; Adsorption; Separation membrane.

1. Introduction

Graphene is a rapidly rising star in the fields of condensed matter physics and materials science. It is a two-dimensional material with a single-atom thickness, consisting of a lattice structure of closely packed sp2 hybridized carbon atoms, possessing a wide range of application scenarios and representing an advanced material [1]. On October 22, 2004, Kostya S. Novoselov and Andre K. Geim from the Department of Physics at the University of Manchester published a sensational article in Nature Materials, introducing the two-dimensional carbon material and its special properties to academia and industry for the first time, and named the newly discovered structure graphene[2].

With the rapid development of the petrochemical, metal smelting, and dye industries, the global annual discharge of oily wastewater reaches as high as 9 to 14 billion cubic meters, and the treatment steps are cumbersome, requiring significant manpower, material, and financial resources[3]. Therefore, selecting efficient oil-water separation adsorbents is crucial. Graphene itself possesses excellent physical and chemical properties and has enormous potential in the field of oil-water separation. Its various modified composite materials further provide a wide range of options for oily wastewater treatment. Consequently, research on graphene oxide composite materials is of significant importance for the oil-water separation field and can bring great value in practical production.

This review mainly involves a careful study of literature from other researchers and summarizes the preparation processes and oil-water separation performance test results of the products they studied, aiming to provide readers with a general understanding of the progress of some graphene oxide composite membranes in the field of oil-water separation in recent years.

2. Application of Graphene Oxide (GO) Membranes in Oil-Water Separation

Graphene oxide (GO) membranes have broad application prospects in oil-water separation scenarios. GO membranes possess a unique two-dimensional single-layer structure, rich in oxygen-containing functional groups such as hydroxyl and carboxyl groups. These characteristics make them highly dispersible in water, resistant to fouling, and easy to functionally modify [4].

2.1. Ethylenediamine Cross-linked Graphene Oxide Membrane

Li et al. used ethylenediamine to cross-link GO, and after freeze-drying treatment, obtained an ethylenediamine-modified GO aerogel. This aerogel was then compressed into a membrane under a pressure of 6 MPa, resulting in a novel cross-linked GO membrane. This membrane exhibits high flux (225 L/(m²·h)) and good oil-water separation performance for various oil-water emulsions. Specifically, the separation efficiency for soybean oil-water emulsion can reach as high as 99.93%[5].

2.2. Graphene Oxide/Polyacrylonitrile Fiber Hierarchical Composite Membrane (GO/APAN)

According to Liu et al., relaying on the research of Yue and Zhang et al.: "The graphene oxide/polyacrylonitrile fiber hierarchical composite membrane (GO/APAN) is a composite membrane produced by electrospinning, featuring a highly interconnected pore structure, high porosity (>90%), adjustable functionality, and good structural stability." Its preparation process is shown in Figure 1[6].

(a)Preparation of PAN membrane via electrospinning technology; (b)Synthesis of APAN membrane by reaction with diethylenetriamine;(c)Preparation of GO/APAN membrane by modification with GO[7]

Firstly, a PAN membrane was prepared by electrospinning, then reacted with diethylenetriamine (DETA) to introduce NH2 groups onto the fiber surface, and lastly, GO was introduced through acylation and nucleophilic reactions to prepare the modified PAN (APAN) membrane. Subsequently, Zhang et al. measured the flux of PAN, APAN, and GO/APAN membranes using a continuous cross-flow separation system

and studied the influence of the composite membrane's hydrophilicity and morphology on separation performance through ultrasonic treatment.

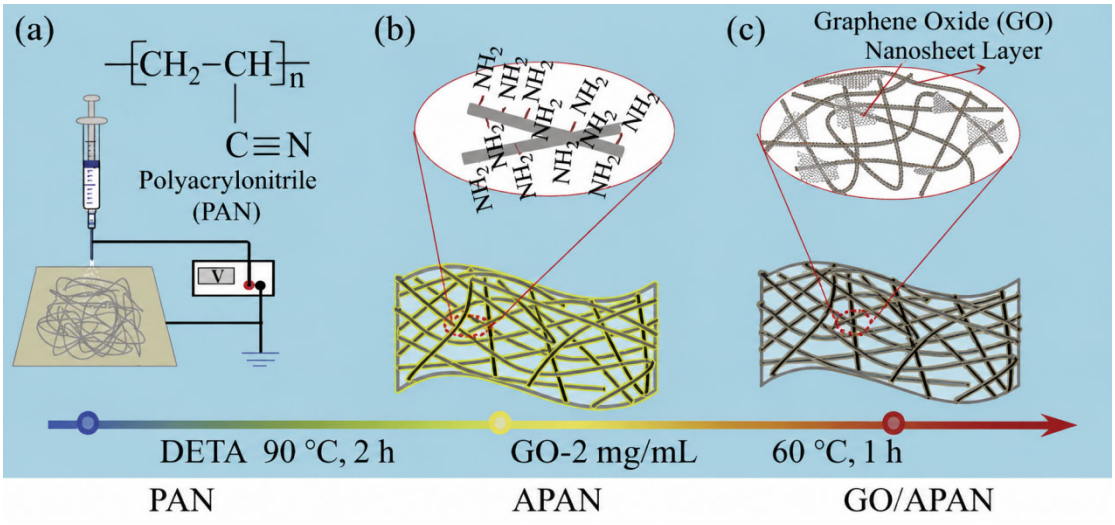


Figure 1. Design and preparation process of the GO/APAN composite membrane

The research results showed that the GO/APAN composite membrane possesses superhydrophilicity and anti-fouling properties, along with very high flux (~10000 LMH). In oil/water emulsion separation experiments, it achieved high oil-water separation performance (98%). The ultra-high flux of the GO/APAN composite membrane is attributed to its high porosity, while the outstanding oil-water separation performance is due to the smaller GO sheets modified on the APAN fibers and the larger GO sheets connecting the APAN fibers.

2.3. GO/ATP Membrane (GOAP Membrane)

The GOAP membrane is a GO-modified membrane prepared on the surface of a ceramic substrate (Al_2O_3 ceramic sheet) by introducing polyvinyl alcohol (PVA) and attapulgite (ATP) into the interlayers of GO sheets.

Cheng's research elaborates on the preparation of the GOAP membrane and the methods for testing its oil-water separation performance. The preparation process of the GOAP composite membrane is shown in Figure 2, with the specific steps as follows:

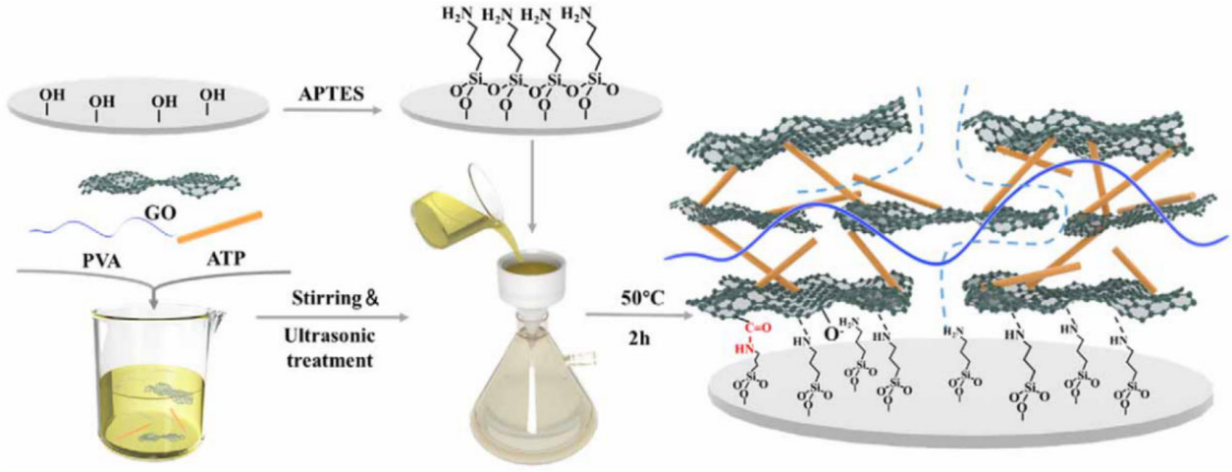


Figure 2. Preparation flow chart of the GOAP composite membrane

"(1) Take a small amount of PVA into a beaker with deionized water, heat in a water bath at 95°C while stirring, and prepare a solution with a mass concentration of 1 wt%.

(2) According to the required membrane overall ratio, take appropriate amounts of GO dispersion, ATP dispersion, and PVA solution respectively, mix them, and dilute to 75 mL.

(3) Stir the mixture for 30 min, then transfer to ultrasonic treatment for 30 min to achieve uniform dispersion. Finally, vacuum filter the solution onto the pretreated Al_2O_3 substrate to obtain the GOAP-X composite membrane (where X is the mass ratio of ATP/GO), and place it in a 50°C oven to dry overnight."

Cheng measured the water flux and anti-fouling performance of the modified membrane using a self-made cross-flow device (Figure 3):

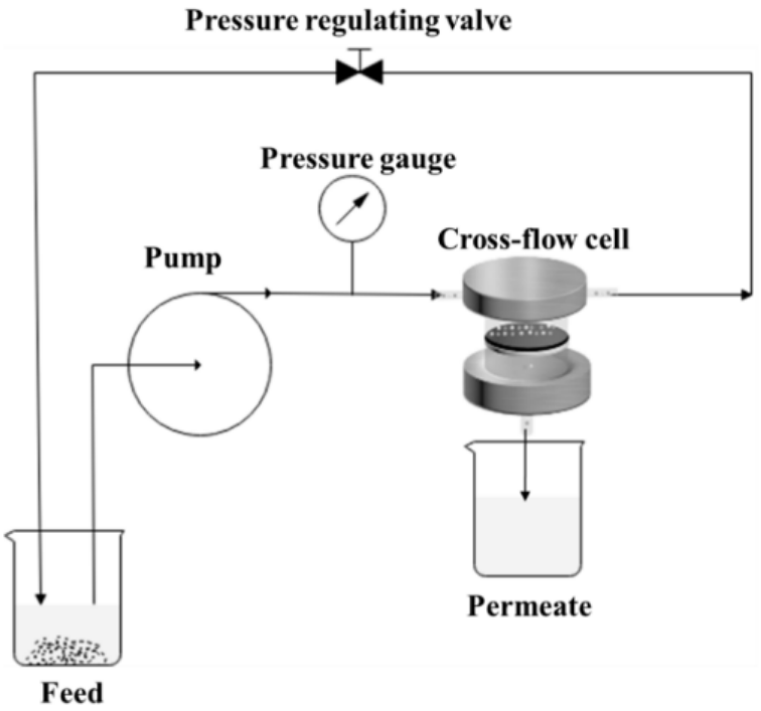


Figure 3. Schematic diagram of the cross-flow filtration system

After a series of measurements and experiments, it was concluded that the pure water flux of the GOAP membrane reached 16.16 L/(m²·h), the rejection rate remained above 99%, and the membrane flux recovery rate could reach up to 83.31%, thus demonstrating the GOAP membrane's capability to treat oil-water emulsions [8].

2.4. Magnetic ZIF-8/Graphene Aerogel

Chen et al. prepared a magnetic ZIF-8/graphene aerogel and conducted a series of oil-water separation performance tests on it [9]. The general preparation method is as follows:

(1) Preparation of magnetic nickel ferrite: $NiFe_2O_4$ was prepared by a hydrothermal method. A certain amount of $FeCl_3 \cdot 6H_2O$ and $NiSO_4 \cdot 6H_2O$ was weighed and dissolved in deionized water, magnetically stirred for 10 min. NaOH solution was added to the above mixed solution and stirred continuously until uniform. The hydrothermal reaction was carried out at 180°C for 10 h. The product was then washed three times each with deionized water and anhydrous ethanol, and vacuum-dried for 24 h to obtain $NiFe_2O_4$.

(2) Preparation of ZIF-8: ZIF-8 crystals were prepared using a room-temperature solution precipitation method. A certain amount of $Zn(NO_3)_2 \cdot 6H_2O$ in methanol solution was slowly added to a methanol solution containing a certain amount of 2-methylimidazole, vigorously stirred for 1 h, and allowed to stand for reaction for 24 h. After washing three times with methanol, the product was vacuum-dried for 14 h to yield ZIF-8.

(3) Preparation of GA: Graphene aerogel was prepared using an improved chemical reduction method [10]. 160 mg of L-ascorbic acid was dissolved in 4.0 mL of graphene oxide dispersion at different concentrations, 11.0 mL of deionized water was added, and then ultrasonically dispersed uniformly. The mixture was heated at 95°C for 60 min to obtain a graphene hydrogel. After washing three times with deionized water and freeze-drying, GA was obtained.

(4) Preparation of GA/$NiFe_2O_4$/ZIF-8 composite aerogel: The composite aerogel was prepared using a chemical reduction method [11]. 10.0 mg of magnetic nickel ferrite and different masses of ZIF-8 were added to the graphene dispersion to prepare four composite aerogels with different mass ratios. With x representing the mass of ZIF-8 added, the products were named GA/$NiFe_2O_4$/ZIF-8-x (x being 8.0 mg, 12.0 mg, 16.0 mg, and 20.0 mg, respectively). 160 mg of L-ascorbic acid and a certain amount of $NiFe_2O_4$ were weighed and dissolved in 16 mL of 1 mg/mL graphene dispersion, followed by ultrasonic treatment until uniform. The previously synthesized ZIF-8 was dissolved in 3.5 mL of methanol and added to the mixed solution. After vigorous shaking for 5 times, the mixture was placed at 95°C for 1 h to obtain a bulk hydrogel. After washing several times with deionized water and freeze-drying, the GA/$NiFe_2O_4$/ZIF-8 composite aerogel was obtained.

Subsequently, the team conducted a series of analyses on the product, including infrared spectroscopy, X-ray diffraction analysis, thermal stability analysis, specific surface area analysis, and scanning electron microscopy analysis. In terms of the product's oil-water separation application, adsorption capacity analysis, selective oil absorption analysis, cyclic usability performance analysis, and thermal stability analysis were also performed, ultimately drawing a series of conclusions:

(1) The series of GA/$NiFe_2O_4$/ZIF-8 composite aerogels with different mass ratios exhibit higher thermal stability and specific surface area compared to GA.

(2) The product demonstrates high adsorption capacity for five organic solvents: ethanol, n-hexane, oleic acid, peanut oil, and vacuum pump oil, far exceeding that of GA.

(3) The product has a high reuse rate. After 5 cycles, the oil-water adsorption and separation effect of the composite aerogel shows no significant change, with the decrease in adsorption capacity ranging from 1% to 6%.

(4) Within a certain temperature range (-60°C to 140°C), the product maintains its efficient adsorption performance, proving its good thermal stability.

2.5. Superhydrophobic Lignin/Graphene Oxide Aerogel

Jiang conducted a detailed study and explanation on the preparation and oil-water separation performance of the superhydrophobic lignin/graphene oxide aerogel. The preparation of this product generally involves the following steps:

(1) Dissolve sodium lignosulfonate in deionized water to prepare a suspension with a concentration of 2.4 mg/mL. Then, mix a sodium tripolyphosphate solution with a concentration of 0.8 mg/mL with the suspension in a 1:1 ratio, followed by stirring for 15 min to obtain lignin nanoparticles in suspension (LSs).

(2) Disperse graphene oxide powder with deionized water for 30 min and ultrasonicate for 45 min to create a suspension with a mass concentration of 5 mg/mL. Subsequently, add 10 mL of LSs and 0.8 g of ethylenediamine (EDA) to the suspension, stir for 1 h. Then, transfer the mixed solution into a reaction kettle with a polytetrafluoroethylene liner. React at 200°C for 24 h to obtain a GO/LSs/EDA hydrogel. Purify the hydrogel by immersion in deionized water, then freeze-dry for 48 h to produce the lignin nanoparticle/reduced graphene oxide aerogel (LNGA). Using the exact same experimental procedure as above, prepare the reduced graphene oxide aerogel (NGA) without the addition of lignin nanoparticles.

(3) Place the LNGA and 0.4 mL of methyltrimethoxysilane (MTMS) in a sealed container and react in a 105°C oven for 10 h. Then, adjust the oven temperature to 60°C and continue the reaction for 24 h to remove the remaining silane and obtain the highly hydrophobic aerogel MLNGA. The preparation process of MLNGA is schematically illustrated in Figure 4.

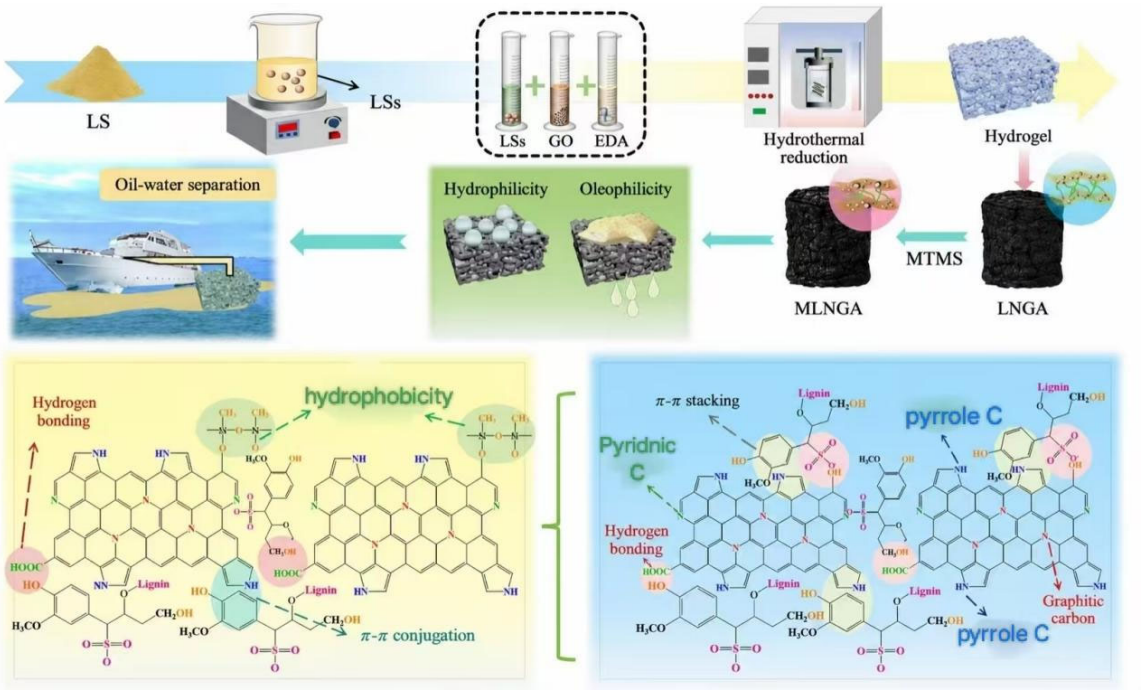


Figure 4. Schematic diagram of the preparation principle of MLNGA

After obtaining the product, Jiang conducted a series of performance tests on it and finally concluded: The separation flux of this product reaches as high as 43209.71 L/(m²·h), with a separation efficiency of ~99% in a continuous oil-water separation device, and also possesses good oil absorption capacity (22-58 g/g) [12].

3. Performance Comparison of Graphene Oxide Composite Membranes

Water flux and oil rejection rate are important reference factors for evaluating composite membrane performance. Table 1 compares the flux and oil-water separation performance of the various graphene oxide composite membranes prepared by different methods mentioned above. Researchers enhanced the oil-water separation performance of the membranes by modifying GO membranes with materials such as ethylenediamine, ceramic substrates, and lignin.

Table 1. Separation performance of different modified graphene composite membranes

Modification method	Water flux/[L/(m²·h)]	Oil rejection rate/%
Ethylenediamine Cross-linked Graphene Oxide Membrane	225	99.93
GO/APAN	10000	99
GO/ATP	16.16	99
MLNGA	43209.71	99

Among them, the magnetic ZIF-8/graphene aerogel was not measured for water flux and oil rejection rate using conventional methods but was evaluated using other indicators; therefore, it is not listed in the table, but it also possesses excellent performance.

Regarding the water contact angle, MLNGA exhibits 148.85°, while GO/ATP increases the water contact angle with a higher proportion of ATP, which can even exceed 150°.

4. Summary and Outlook

Graphene oxide membranes inherently possess excellent potential for oil-water separation, especially favored for their unique structure, high cost-effectiveness, and stability, and are widely applied in the oil-water separation field. Researchers have effectively improved the various properties of GO membranes through physical and chemical modifications. Although significant progress has been made in GO membrane research, some issues still require more in-depth investigation. Particularly, studies on GO membranes are mostly conducted in laboratory environments and lack practical testing experience under industrial conditions. This could lead to significant discrepancies in results, which may even be less than ideal. Therefore, to widely apply GO composite membrane research in practical industrial fields, the key factors of oil-water separation should be grasped more accurately, and the actual application scenarios should be replicated as closely as possible. In summary, graphene oxide composite membranes have very promising application prospects, but further research is still needed.

Future research on graphene oxide (GO) composite membranes can focus on the following directions:

(1) Stimuli-responsive composite membranes: enabling GO composite membranes to be controllably regulated by external stimuli such as temperature, light, and pH.

(2) Controllable interlayer spacing: investigating methods to precisely tune and control the interlayer spacing of the membranes.

(3) Design of highly stable and anti-swelling composite structures: since GO membranes are prone to swelling and structural instability in aqueous environments, it is necessary to develop strategies to ensure long-term membrane stability.

References

[1] Geim, A. K., & Novoselov, K. S. (2007). The rise of graphene. Nature Materials, 6(3), 183–191. https://doi.org/10.1038/nmat1849

[2] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., & Firsov, A. A. (2004). Electric field effect in atomically thin carbon films. Science, 306(5696), 666–669. https://doi.org/10.1126/science.1102896

[3] Wang, M. Y., Wang, Z. Q., & Tian, M. (2020). Discussion on the hazards and effective treatment of oily wastewater. Environment and Development, 32(5), 58–60. (In Chinese)

[4] Huang, G. J., Chen, Z. G., Li, M. D., et al. (2016). Surface functional modification of graphene and graphene oxide. Acta Chimica Sinica, 74(10), 789–799. (In Chinese with English abstract). https://doi.org/10.6023/A16050242

[5] Li, G. F., Wang, X., Tao, L., et al. (2015). Cross-linked graphene membrane for high-performance organics separation of emulsions. Journal of Membrane Science, 495, 439–444. https://doi.org/10.1016/j.memsci.2015.08.031

[6] Liu, Y. C., Niu, W., Wang, Q., et al. (2021). Research progress on graphene oxide composite membranes for oily wastewater treatment. Environmental Protection of Oil & Gas Fields, 31(4), 11–17. (In Chinese)

[7] Zhang, J. Q., Xue, Q. Z., Pan, X. L., et al. (2017). Graphene oxide/polyacrylonitrile fiber hierarchical-structured membrane for ultra-fast microfiltration of oil-water emulsion. Chemical Engineering Journal, 307, 643–649. https://doi.org/10.1016/j.cej.2016.08.108

[8] Chen, A. W. (2022). Preparation of ceramic-based graphene oxide composite membrane and its oil-water emulsion separation performance [Doctoral dissertation]. Beijing University of Chemical Technology. https://doi.org/10.26939/d.cnki.gbhgu.2022.001041

[9] Chen, Z. X., Meng, F. L., Zhang, L. D., et al. (2024). Preparation of magnetic ZIF-8/graphene aerogel and its oil-water separation performance. Polymer Materials Science and Engineering, 40(4), 137–146. https://doi.org/10.16865/j.cnki.1000-7555.2024.0083

[10] Kuruahmet, D., Singil, M. M., Guler, A., et al. (2023). Enhancing the electrochemical properties of silicon nanoparticles by graphene-based aerogels. Energy Technology, 11, 2201503. https://doi.org/10.1002/ente.202201503

[11] Mao, J. J. (2018). Preparation of MOFs/graphene aerogel and its application in water pollution and air pollution [Doctoral dissertation]. Soochow University.

[12] Jiang, H. (2025). Preparation of superhydrophobic lignin/graphene oxide aerogel and its oil-water separation performance [Doctoral dissertation]. Xinjiang Agricultural University. https://doi.org/10.27431/d.cnki.gxnyu.2025.000506