

Research Progress on the Application of Nitrogen-Doped Three-Dimensional Graphene Hydrogels in Water Environment Pollution Remediation

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ABSTRACT

With the rapid development of the chemical industry, a large amount of industrial wastewater is also produced, which contains a large amount of organic matter with high chemical stability and difficult to be biodegraded, such as acids, alkalis, salts, organic solvents, toxic dyes and heavy metal ions, which is very detrimental to the protection of natural ecology and the maintenance of human health. As a two-dimensional material, graphene's sp² hybridized carbon atomic structure can produce π - π interactions with organic dye pollutants containing benzene ring structures, thereby adsorbing pollutants. Assembling two-dimensional graphene into a hydrogel with a three-dimensional network structure can further increase the contact area with pollutants and improve the adsorption of pollutants. This paper mainly discusses the research progress of the application of nitrogen-doped three-dimensional graphene hydrogels (NGHs) in water environment pollution remediation.

KEYWORDS

Nitrogen-Doped Graphene, Graphene Hydrogel, Water Environment Remediation, Sewage Treatment, Graphene Preparation.

1. INTRODUCTION

In response to current sustainability and environmental standards, it is an important mission for scientific researchers to develop adsorbent materials with high specific surface area, high efficiency and easy recycling. This field is also the focus of research on environmental functional materials.

3D graphene combines the structural advantages and unique properties of 2D graphene sheets, including huge specific surface area, excellent chemical stability, superconductivity and thermal conductivity [1-4]. Its porous structure and wide specific surface area provide ample space for the adsorption of pollutant molecules, while its internal pore network promotes the diffusion of pollutant molecules, improves mass transfer efficiency, and accelerates the adsorption reaction kinetics. At the same time, its stable chemical properties, excellent electrical conductivity and thermal conductivity enable it to be recycled through environmentally friendly electrochemical methods and thermal treatment.

As a typical 3D structure, hydrogel is composed of a fluffy porous network and is suitable for electrochemical, catalytic, sensing and water treatment applications, especially industrial wastewater treatment [5]. Hydrogel contains polar or hydrophilic groups such as -OH, -NH₂, -SO₃H or -COOH, which bind to water molecules through hydrogen bonds or electrostatic interactions, show good swelling properties, and can effectively absorb water and dyes, creating conditions for the dye degradation process. Therefore, combining hydrogel with 3D graphene will significantly enhance its ability to photocatalytically decompose pollutants.

This article discusses in detail the preparation methods of N-doped 3D graphene hydrogels (NGHs), as well as the cutting-edge exploration and current achievements of this innovative material in the field of environmental adsorption. The article also deeply analyzes the current research trends in the preparation process and adsorption performance of NGHs, and specifically points out potential problems and possible future development trends.

2. PREPARATION OF NGHS

2.1. Chemical Vapor Deposition(CVD)

Chemical vapor deposition (CVD) is one of the commonly used techniques for constructing 3D graphene with an ordered layered structure and precise dimensions. This method involves forming 3D graphene on a specific template such as nickel foam or copper foam under a high temperature and high pressure gas environment. Referring to Figure 1, CHEN et al. [6] used the CVD strategy to synthesize 3D graphene foam. Other researchers creatively used shells as templates to produce ultra-light (3 mg cm^{-3}), extremely tough and conductive 3D graphene. Even after 200 mechanical bends, the resistance remained stable[7].The CVD method shows significant advantages in the manufacture of 3D graphene. It can flexibly control the density and structure of the material and produce 3D graphene with fewer defects. However, its disadvantages are that it requires a high temperature environment and inert gas, and the related equipment is expensive, which limits large-scale production and poses a certain obstacle to its practical application. In the production of nitrogen-doped graphene, the CVD method can effectively incorporate nitrogen atoms by finely controlling the reaction conditions and precursors. The resulting nitrogen-doped graphene has high quality, large surface area and excellent uniformity, and therefore has broad application prospects in electronic equipment and other fields.

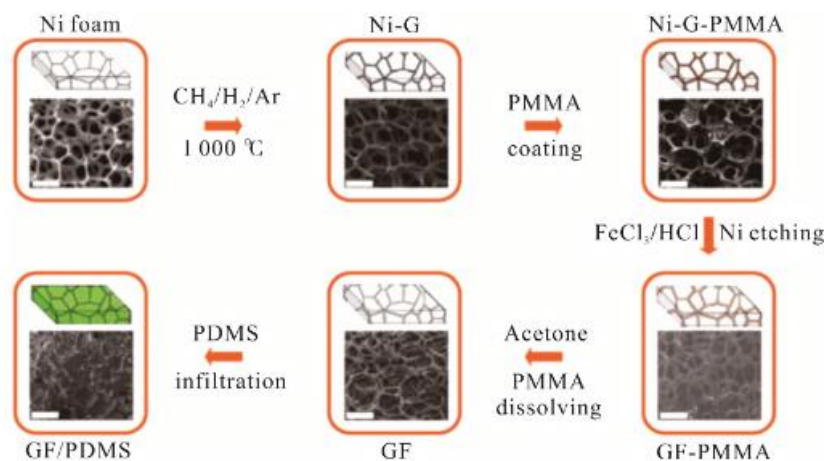


Fig. 1 Synthesis of graphene foam (GF) and its composite with PDMS

2.2. Plasma treatment

Plasma effects play a key role in graphene surface modification technology. By finely controlling the working characteristics of plasma, such as its energy output, gas type, and flow rate, it is possible to achieve a deep and precise nitridation process of the carbon layer[8] . This nitrided graphene derivative exhibits excellent electronic and magnetic properties, especially in the field of energy conversion and storage, showing unprecedented application prospects.

2.3. Hydrothermal synthesis

The regulation of chemical reactions in a solution environment is a key technology that involves driving the transformation of reactants by means of heating and pressure to produce a predetermined target product. Among the strategies for the generation of NGHs, solvothermal and hydrothermal synthesis have successfully achieved the effective embedding of nitrogen due to their flexibility, such as the precise selection of solvents, reaction components and conditions[9]. This method has become a popular choice in research laboratories and the industry due to its intuitive operation process, economical cost-effectiveness and potential for large-scale production. In 2010, Shi Gaoquan's team at Tsinghua University reported in *Nature Materials* that they used hydrothermal reduction technology for the first time to convert high-concentration graphene oxide into macroscopic reduced graphene oxide (rGO) hydrogel. This breakthrough work is clearly shown in Figure 2[10]. In this process, graphene oxide (GO) undergoes a deoxygenation reduction in a high-temperature and high-pressure environment and is converted into rGO. At the same time, the strong π - π interaction between rGO layers enables them to form a three-dimensional graphene-based composite material. Since then, hydrothermal reduction has played an important role in the construction of three-dimensional graphene composite gel materials.

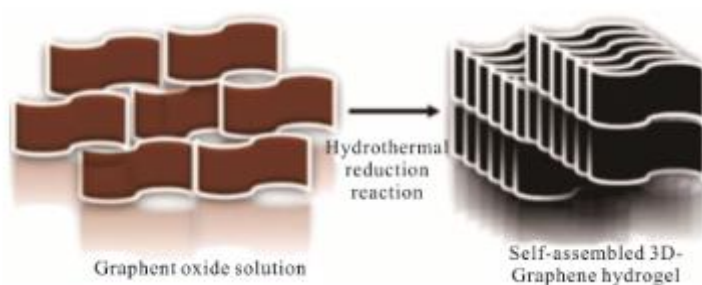


Fig. 2 Preparation of 3D graphene hydrogel by hydrothermal reduction method

2.4. Heat treatment

The process of chemically transforming the graphene surface through high-temperature heat treatment to form nitrogen-doped graphene is simple, but it often requires high temperature and long time, and the yield is not high, so it encounters obstacles in its widespread application. Although each method has its own advantages, it is also accompanied by specific limitations.

In recent years, an innovative strategy is to use various nitrogen sources and binders and reducing agents to generate nitrogen-doped graphene hydrogels with adjustable doping concentrations through hydrothermal reactions. This method can be completed at relatively low temperatures and pressures, and can precisely control the nitrogen doping level to customize graphene materials with different properties. In addition, nitrogen-doped graphene hydrogels have significant advantages. First, they have excellent mechanical strength and can withstand strong external forces, ensuring stability in various applications. Secondly, their light weight provides a broad space for applications in energy, aerospace and other fields. Finally, due to the incorporation of nitrogen atoms, nitrogen-doped graphene hydrogels perform well in adsorption and photocatalytic properties, which gives them great application potential in the fields of environmental protection and energy conversion.

3. APPLICATION OF NITROGEN-DOPED THREE-DIMENSIONAL GRAPHENE HYDROGEL IN SEWAGE TREATMENT

3.1. Treatment of dye wastewater

Cationic dyes exist in the form of cations in water and are mainly used for dyeing acrylic fibers. NGHs show excellent adsorption efficiency for such dyes, and their adsorption capacity exceeds that of traditional adsorbent materials. NGHs contain abundant deprotonated hydroxyl and carboxyl groups, resulting in a high density of negative charges on their surface [11-12]. Therefore, electrostatic attraction is the main mechanism for NGHs to adsorb cationic dyes. However, the adsorption of dyes by NGHs is easily affected by the pH value of the solution, and the adsorption capacity is weakened when the pH value is low. The electrostatic force of NGHs is regulated by the point of zero charge (pHpzc). When the pH value exceeds pHpzc, the carboxyl and hydroxyl groups lose protons, and the surface of NGHs presents a net negative charge, which is conducive to the adsorption of cationic dyes. On the contrary, if the pH value is lower than pHpzc, the net charge on the surface of NGHs becomes positive, and the repulsion between like charges will reduce the amount of dye adsorption. SHI Yacheng et al. [13] used glutathione to modify graphene oxide and prepared nitrogen-sulfur co-doped three-dimensional graphene hydrogel (N/S-GH). This material exhibits excellent adsorption performance for organic dyes (such as methylene blue, malachite green and crystal violet) in an aqueous environment, especially for malachite green, with an adsorption amount of up to 806.5 mg·g⁻¹ at 313K, and after six adsorptions, the recovery rate remains almost 100%.

Anionic dyes exist as anions in aqueous media and include direct dyes and acidic pigments. They are designed for coloring materials such as cotton fibers and silk. In order to effectively use electrostatic attraction to promote the adsorption of such dyes in wastewater by NGHs, it is often necessary to attach positively charged functional groups to the surface of graphene nanosheets, such as embedding compounds containing amine groups. Chen et al. [14] cleverly used the synergistic effect of -NH₂-rich chitosan (CS) and graphene oxide (GO) to construct a 3DGM hydrogel adsorbent specifically for eosin Y anionic dyes. Its excellent adsorption performance reached a capacity of up to 230 mg per gram. The schematic diagram of this process is shown in Figure 3, showing a high adsorption effect.

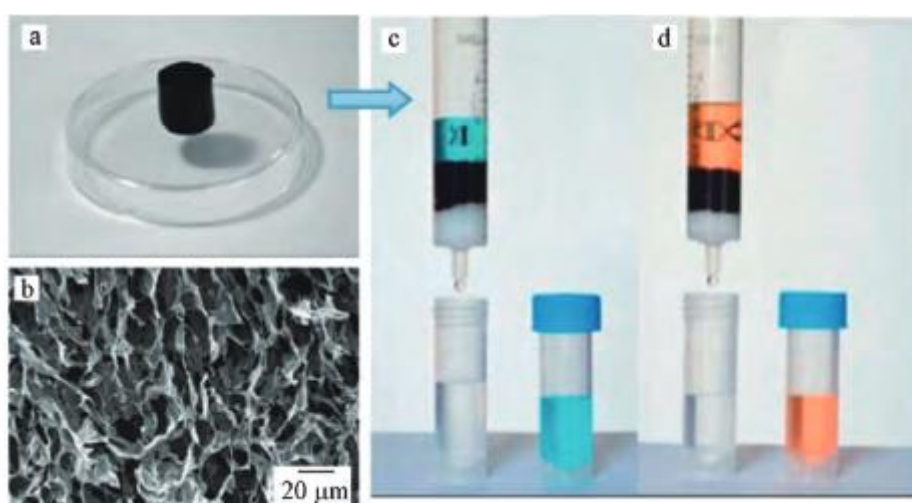


Fig. 3 (a) 3DGM; (b) SEM of 3DGM; (c) MB removed from 3DGM; (d) Photograph of 3DGM removed from potato red Y

3.2. Adsorption of metal ions

Heavy metal ions in industrial wastewater, such as copper, zinc, and nickel, pose a serious threat to the ecological environment and human health. Therefore, it is crucial to ensure that their discharge meets environmental standards. NGHs show strong adsorption properties for heavy metal ions. The introduction of nitrogen atoms gives the hydrogel surface an additional negative charge, enhancing the electrostatic attraction effect with cations [15]. At the same time, the three-dimensional network structure provides abundant adsorption sites for metal ions, significantly improving the adsorption efficiency. Therefore, NGHs show significant application potential in the treatment of wastewater containing heavy metal ions. Researchers Lei et al. [16] synthesized NGHs by chemical vapor deposition, which can effectively adsorb a variety of heavy metal ions, such as Zn^{2+} , Fe^{3+} , Pb^{2+} , and Cd^{2+} . The experimental data of the adsorption effect and the number of cycles are shown in Figure 4. It is worth noting that the adsorption performance of NGHs will increase with the decrease of the pH value of the background solution. When the pH value is low, H^+ will compete with heavy metal ions for the carboxyl and hydroxyl positions on the graphene surface, resulting in a decrease in adsorption capacity. In addition to pH, the concentration of other cations (such as Ca^{2+} , Mg^{2+}) in the background solution and the solution temperature will also affect the adsorption capacity and the formation of NGHs. These cations will compete with the main adsorbed metal ions for limited oxygen-containing functional groups and inhibit their ionization on the surface of NGHs, thereby limiting the adsorption of heavy metal ions. In order to accurately evaluate the adsorption performance of NGHs for metal ions, pretreatment methods such as adjusting the pH value, boiling the solution or using metal ion chelators can effectively remove the background ions Ca^{2+} and Mg^{2+} and ensure the purity of the experimental conditions [17].

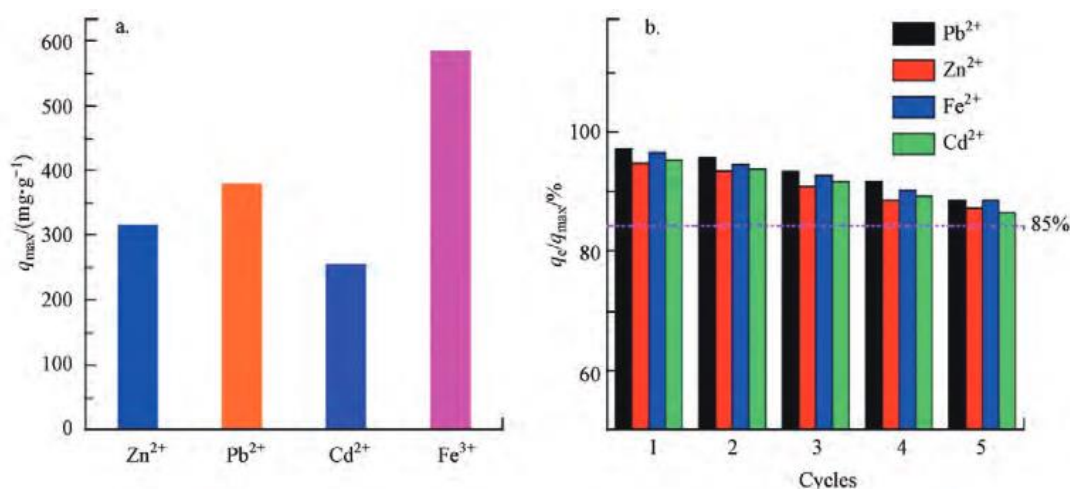


Fig. 4 (a) Maximum adsorption capacity of NGHs for metal ions; (b) Adsorption cycle number of NGHs for metal ions

In addition, the additional electric field effect will also profoundly affect the performance of NGHs in adsorbing metal ions. Wei et al. [18] prepared NGHs by a hydrothermal method, which showed excellent Pb^{2+} adsorption characteristics under the action of an external electric field, with a maximum adsorption capacity of up to 650.4 mg/g. The significant adsorption effect of this gel on Pb^{2+} is mainly attributed to the following key factors: (1) the electromagnetic attraction of the external electric field to Pb^{2+} ; (2) the charge interaction between nitrogen-doped graphene and Pb^{2+} ; (3) the ultra-high specific surface area of the gel; and (4) the coordination between nitrogen atoms and Pb^{2+} . It is particularly worth mentioning that even after 100 consecutive cycles, the removal efficiency of the hydrogel for Pb^{2+} decreased by only 5%, showing a cyclic stability far exceeding that of conductive polymers and their composite materials with graphene.

3.3. Adsorption of oil

The hydrophobic surface and lipophilic core structure of NGHs make them have excellent oil adsorption performance. Pollutants can be embedded in the hydrogel and effectively separated from water. This three-dimensional structure not only provides sufficient storage space, but also facilitates the recovery and subsequent treatment of pollutants after saturation, showing great potential in oil pollution treatment. The research team of LIU [19] synthesized a 3D nitrogen-boron co-doped graphene (BN-GAs) using solvothermal and freeze-drying technology. In the experiment, they observed that graphene could quickly adsorb Sudan red-dyed dodecane in a very short time, making the water surface instantly clear. They found that the adsorption capacity of the material for different oils and organic solvents was significantly different, up to 23 times, and the adsorbed oil could be reused after acetone extraction, and the material itself could still be reused after drying. Another study conducted by Zhao et al.[20] prepared N-doped ultralight three-dimensional graphene-pyrrole composite (3DGM) by reaction in an autoclave. In this process, pyrrole not only served as a nitrogen source and swelling agent, but also gave the gel unique fire resistance, conductivity and non-metallic catalytic properties. The gel exhibits excellent reversible adsorption properties, with adsorption capacities of up to 270 mg/g for gasoline and 460 mg/g for olive oil. Its excellent mechanical strength allows it to be recycled multiple times by simple extrusion, without the need for complex recycling steps.

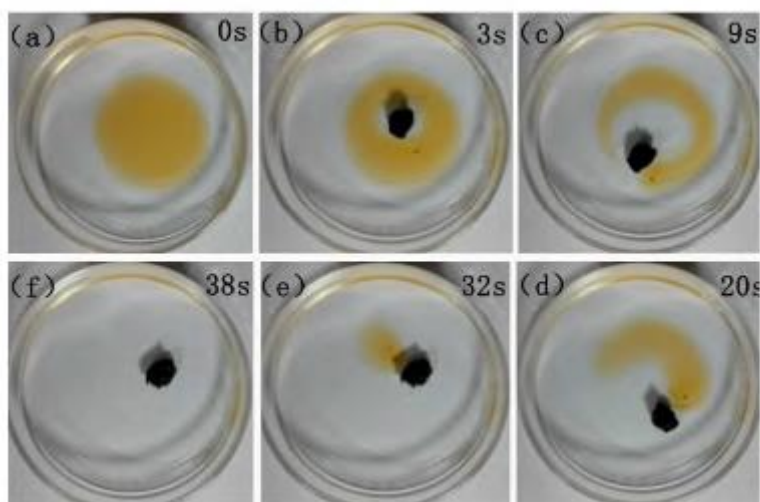


Fig. 5 BN-Gas absorbs dodecane from water (dodecane is dyed with Sudan red)

4. CONCLUSION

In recent years, various material synthesis techniques, such as chemical vapor deposition (CVD), plasma treatment, solvothermal and hydrothermal methods, have been used to manufacture NGHs, and these materials have shown significant adsorption performance in removing pollutants such as dyes, heavy metal ions, oils and antibiotics from wastewater. However, as an emerging adsorption medium, the research and development and water treatment application of NGHs are still in the early stages and face several challenges. First, the current manufacture of 3NGHs usually involves expensive raw materials and equipment, and the process is both complex and potentially risky. Therefore, reducing costs is a key challenge. Secondly, the existing NGHs preparation methods are limited to laboratory scale and cannot be adapted to large-scale production, which seriously hinders its commercialization process. It is urgent to develop synthetic technologies suitable for industrialization. Furthermore, pore structure and porosity play a decisive role in the adsorption performance of NGHs, but current technology cannot accurately control these parameters, so it is necessary to deepen the research on controllable synthesis technology of NGHs. Finally, the research

on the adsorption performance of NGHs is mostly focused on a single type of pollutant, and it is particularly urgent to expand the application research to complex polluted environments to promote the practical application of such materials.

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