Preparation and Photocatalytic Properties of Graphite-Phase Carbon Nitride Materials

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Abstract. As a new semiconductor material, graphite-phase carbon nitride can be effectively used in the utilization of renewable energy and environmental pollution control. Because the preparation of graphite-phase carbon nitride is complicated with different optimization strategies in various industrial fields, the preparation and modification of graphite-phase carbon nitride are summarized in this paper. Combined with the excellent performance of graphite-phase carbon nitride in the band gap, specific surface area and stability, the research status of its modified materials in the photocatalytic hydrogen production, degradation of organic pollutants and antibacterial is analyzed. Finally, the future development trend of graphite-phase carbon nitride materials is prospected.

Keywords: Graphite-Phase Carbon Nitride; Heterojunction; Photocatalytic Hydrogen Production; Photocatalytic Degradation; Antibacterial.

1. Introduction

With the increasing demand for energy, limited traditional energy can no longer meet the long-term needs of human beings. At the same time, traditional fossil energy such as coal and oil will produce toxic gases after use, which will destroy the ecology and aggravate environmental deterioration. Therefore, a large number of researchers are devoting themselves to the research on new green energy and efficient treatment of environmental pollutants.

Photocatalytic technology can use solar energy as energy for production and environmental governance. It is a new green technology with important application prospects in the fields of energy and environment. Its basic principle is that semiconductor materials undergo electronic transitions under illumination, forming electron-hole pairs, and then producing strong oxidizing radicals. On this basis, graphite-phase carbon nitride (g-C₃N₄) as a new type of semiconductor material has attracted many researchers due to its excellent performance in photocatalysis and various application prospects. For example, Wang prepared and used g-C₃N₄ in the mesoporous structure as a photocatalyst to produce hydrogen [1]. Liu used the g-C₃N₄ modified by quaternary ammonium salt to conduct photocatalytic sterilization experiments on Acinetobacter baumannii and Staphylococcus aureus [2]. Yin et al. took advantage of the defect g-C₃N₄ to degrade organic dyes such as methyl orange, RhB, and methylene blue [3]. However, g-C₃N₄ still has problems such as a small specific surface area, poor electrical conductivity, high recombination rate of photogenerated carriers, and difficulty in absorbing light with wavelengths greater than 460nm. To further improve the performance of g-C₃N₄ in practical applications, existing research focuses on optimizing the performance of g-C₃N₄, and the optimization method can be divided into three categories according to three processes of photocatalytic reaction as follows. (1) Regulate the electronic and band structure of g-C₃N₄ to improve the efficiency of the light absorption process. (2) Start in the process of charge transfer. For example, recombine different semiconductors and use the potential difference formed by their different energy band structures to promote the separation of electron-hole pairs. (3) In the stage of surface redox reaction, the surface structure of the photocatalyst material is modified to increase the reaction efficiency.

At present, the application and development of g-C₃N₄ in different fields have not been fully combed. Hence, this paper will not only introduce the preparation method and modification technology of g-
C3N4, evaluate the performance of graphite-phase carbon nitride materials in various application fields, but also focus on summarizing the research results in the direction of photocatalytic hydrogen production, antibacterial and degradation of organic pollutants, and prospect the future development trend of photocatalytic materials g-C3N4.

2. Properties, Preparation and Modification of g-C3N4

g-C3N4 has great potential value, so existing research has focused on improving its application performance through its preparation and modification. Nowadays, the commonly used preparation methods mainly include solid phase synthesis, hydrothermal method, electrochemical deposition method, etc. Besides, the modification technology can be roughly divided into three categories including element doping, morphology regulation and heterojunction construction. This chapter will summarize the preparation and modification process of g-C3N4.

2.1 Basic structure and properties of g-C3N4

g-C3N4 is a non-metallic polymer semiconductor with a layered structure similar to graphite crystals and two basic units including the triazine ring (C3N3) and the 3-s-triazine ring (C6N7). In 2009, Wang et al. first proposed that g-C3N4 has excellent photocatalytic performance. Since then, g-C3N4 has been widely used as a photocatalytic material. He prepared flaky graphite-phase carbon nitride, which enables it to fully absorb light, so it has excellent photocatalytic performance [4]. Zheng prepared nanotube graphite-phase carbon nitride and found that this structure can promote the excitation of electrons in g-C3N4, improve the separation efficiency of electron-hole pairs, and then promote its photocatalytic performance [5]. Moreover, the band gap of g-C3N4 is 2.7 eV, and the wavelength threshold obtained from the Planck formula is about 460nm, so g-C3N4 has the advantage of absorbing visible light compared with traditional semiconductor materials [6]. g-C3N4 has strong thermal stability and chemical stability simultaneously. Due to the effect of aromatic C-N heterocycles, it can still maintain stability in the air at 600°C. The strong van der Waals force between the layered structures makes it maintain chemical stability in most strong acid and base solvents.

2.2 Preparation Method

The preparation methods of graphite-phase carbon nitride mainly include solid-phase synthesis, hydrothermal method, electrochemical deposition method, etc. Examples of various methods will be introduced in detail below with their advantages and disadvantages compared.

The solid-phase synthesis usually chooses to mix a compound with a triazine ring structure with a compound containing nitrogen, which takes place under high temperature and high pressure to obtain g-C3N4. Its most important characteristic is that the product has high crystallinity to prepare g-C3N4 with special morphology. Correspondingly, its reaction conditions are relatively strict.

The hydrothermal method is to use an aqueous solution as a reaction medium to heat the container, so as to dissolve and recrystallize usually insoluble or insoluble substances. It has the advantages of complete grain development and uniform distribution with a low raw material cost. Its disadvantage is that it requires high temperature and high pressure, which makes it have rigorous requirements for equipment. In addition, the hydrothermal method is only suitable for preparing materials not sensitive
to water, which greatly limits its scope of use. To break through its limitations, the solvothermal method came into being.

The solvothermal method uses nitrogen-rich and carbon-rich organic compounds as precursors and dissolves them in organic solvents. By changing the reaction conditions, the morphology of the prepared g-C_3N_4 can be controlled. Compared with the hydrothermal method, the solvothermal method has the advantages of direct and controllable reaction, a more uniform product shape, and a wider application range, but there is still organic solvent pollution that needs to be solved urgently.

Thermal polymerization is to calcine the nitrogen-containing precursor at high temperature, the precursor gradually condensates and removes small molecules, and finally produces g-C_3N_4. Generally, the type of precursor and reaction conditions can significantly affect the physicochemical properties of g-C_3N_4, such as C/N ratio, specific surface area, porosity, light absorption edge and nanostructure. The advantages of thermal polymerization are simple operation, high yield, easy control of product structure and low cost, but the products are generally lumpy, so the specific surface area is small, which has certain limitations on performance.

Electrochemical deposition is a method to prepare g-C_3N_4 thin films by redox reaction of a certain amount of nitrogen-containing organic precursor with an appropriate amount of electrolyte solution under the influence of current density. The electrochemical deposition can synthesize products at room temperature and pressure, which is due to the use of high-nitrogen organic compounds as precursors, reducing the C-N reaction energy barrier. At the same time, it has the disadvantages of low crystallinity and uneven particle size of the product.

In general, each preparation method has its advantages. However, the conventional g-C_3N_4 still has a small specific surface area, weak electrical conductivity, high photogenerated carrier recombination rate, difficulty in absorbing light with wavelengths greater than 460nm and other problems. Therefore, researchers are working on improving its practical application performance in various fields through the modification process.

2.3 Modification Methods

The modification processes of graphite-phase carbon nitride mainly include three categories: element doping, morphology regulation and heterojunction construction. The following will introduce each process in detail with examples.

2.3.1 Non-Metallic/Metallic Element Doping

Element doping is a common method to modify g-C_3N_4, that is, to improve the catalytic efficiency of g-C_3N_4 by doping metal or non-metal elements.

Non-metallic anion doping mainly replaces the C or N atoms in g-C_3N_4, so that its energy bandwidth changes and energy shifts, thereby expanding its visible light response range and improving the efficiency of the light absorption process. For example, Cao prepared porous CN nanosheets (CNO-X) with different oxygen doping amounts [16]. Yang prepared 2-dimensional g-C_3N_4 ultrathin porous nanosheets (TCN-460) with controllable carbon defects and oxygen doping modifications [17].

Alkali metals and transition metals tend to be doped into the framework of g-C_3N_4, resulting in hybridization between the dopant orbital and the molecular orbital of g-C_3N_4. In addition, it leads to changes in the potential of the valence band and conduction band, changing its band structure. Meanwhile, metallic elements can provide free electrons and electron holes simultaneously, so they can increase the carrier concentration and improve the efficiency of their charge transport process. For example, Meng designed and prepared g-C_3N_4 (DN-K-CN) modified by potassium doping and nitrogen defects at the same time. By regulating the concentration of potassium ions, the concentration of nitrogen defects and the amount of potassium doping can be regulated [18].

27
<table>
<thead>
<tr>
<th>Preparation Method</th>
<th>Generalization</th>
<th>Characteristics</th>
<th>Advantage</th>
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<tbody>
<tr>
<td>Solid-Phase Synthesis</td>
<td>The precursor with triazine ring structure and nitrogen source are calcined at 550°C to obtain g-C₃N₄ [7, 8]</td>
<td>Solid-phase synthesis occurs</td>
<td>The product has high crystallinity to prepare g-C₃N₄ with special morphology</td>
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<td>The grain development is complete with a small grain size and uniform distribution; the grain agglomeration is Light with low raw material cost</td>
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<td>Hydrothermal Method</td>
<td>The reaction vessel is heated with water as the heating medium, and the temperature is raised to about 200°C [9, 10, 11]</td>
<td>After mixing the raw materials and heating up, g-C₃N₄ is precipitated by recrystallization</td>
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<tr>
<td>Solvothermal Method</td>
<td>Nitrogen-rich and carbon-rich organic compounds are used as precursors; organic solvents are used as heat conduction media [12]</td>
<td>The precursor is self-assembled by hydrolysis of nitrogen-containing organic compounds</td>
<td>The reaction is direct and Controllable; the product shape is relatively uniform; the scope of application is relatively wide</td>
</tr>
<tr>
<td>Thermal Polymerization</td>
<td>Calcination and polycondensation of nitrogen-containing precursors at high temperatures [13, 14]</td>
<td>Thermal polycondensation using a single precursor without additional nitrogen source</td>
<td>Simple operation; high yield; easy control of product structure; low cost</td>
</tr>
<tr>
<td>Electrochemical Deposition</td>
<td>Electrochemical deposition of nitrogen-containing organics in electrolyte solutions [15]</td>
<td>Redox reaction occurs on the electrode by using the external electric field</td>
<td>Easy to control and can synthesize products under normal temperature and pressure</td>
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It can be seen that the photocatalytic performance of doped g-C₃N₄ has a vital relationship with the type, content and doping mode of the doped elements. Thus, the modification means of element doping can be used in various fields of g-C₃N₄.

### 2.3.2 Morphology Regulation

The external morphology has a great influence on the catalytic properties. At present, the methods of microscopic morphology regulation can be roughly divided into hard template method, soft template method and other non-template method.

The hard template is often used to prepare mesoporous g-C₃N₄, especially using silica as the hard template. Liu used SiO₂ microspheres of different particle sizes as hard templates and melamine as...
raw material to prepare mesoporous g-C_3N_4 with unique macropores and orderly arrangement through thermal polymerization. The prepared samples have a larger specific surface area, providing more active sites for photocatalytic reactions [19]. The hard template can provide g-C_3N_4 with a fixed and adjustable structural framework and pore structure, but its preparation process is cumbersome. Meanwhile, the solution used to remove the template is mostly strong acid, which has great safety hazards [20].

The soft template is similar to the hard template method, but most of the template methods used are surfactants. The precursor and surfactant are mixed to realize self-assembly to prepare materials, and then the template is removed to obtain mesoporous or microporous materials. Mao successfully prepared g-C_3N_4 using triblock polymer PluronicP123 as a soft template method, melamine as raw material, and a concentrated sulfuric acid solution to remove the template [21]. The advantages of the soft template method over the hard template method are that the steps are simpler. There is no need to use toxic and harmful substances to remove the template. However, there are still some shortcomings. For example, the pore structure of the material prepared by the soft template method is disorderly, which will affect the follow-up research.

In addition to the template, some non-template methods such as secondary heat treatment, ultrasonic liquid phase-assisted exfoliation and liquid ammonia-assisted lithiation have also been widely used in the preparation of g-C_3N_4 nanosheets in recent years. For example, Zhang et al. used melamine as raw material, saturated in ethylene glycol solution, and prepared a one-dimensional chain-like g-C_3N_4 by heat-induced polymerization [22].

2.3.3 Heterojunction Construction

Different semiconductor materials have their own advantages and disadvantages. By constructing heterojunctions between metal compounds, carbon materials, halides and other semiconductor materials, their respective monomer defects can be avoided and improved. Meanwhile, a composite catalyst superior to their respective monomers can be generated. According to the band structure of various semiconductors in the complex, the constructed heterojunctions can be roughly divided into type I, type II, type III and type Z (Figure 2.2).

As Wang prepared a double Z-type WS-WO/CNs heterojunction by coupling partially oxidized WS_2 with g-C_3N_4 [23]. Zhu synthesized ZnO/Cu_2O/g-C_3N_4 heterojunction photocatalysts [24]. Liang prepared three kinds of g-C_3N_4/WO_3 heterojunction catalysts by ultrasonic method, calcination method and hydrothermal method respectively [25].

![Figure 2 Four Heterojunctions in Semiconductor Composites](image)

(a)Type I Heterojunction; (b) Type II Heterojunction; (c) Type III Heterojunction; (d) Z-Type Heterojunction

3. Research Progress in Different Scenarios in the g-C_3N_4 Photocatalysis

With its excellent photocatalytic performance, g-C_3N_4 has broad application prospects in various research fields. The three application scenarios that have attracted the most attention from researchers are photocatalytic hydrogen production, degradation of organic pollutants, and antibacterial. This
chapter will introduce the catalytic mechanism of g-C$_3$N$_4$ in the above scenario and list the research results in various fields.

3.1 Photocatalytic Hydrogen Production

As a type of new green energy, hydrogen energy is the focus of research all over the world, but the yield of traditional preparation methods is low, which cannot meet the needs of industrial production. The g-C$_3$N$_4$ material has the advantage of strong light absorption capacity, so it can be used as a photocatalyst in the hydrogen production industry, greatly increasing the yield.

Existing studies have tried to optimize the photocatalytic hydrogen production efficiency of g-C$_3$N$_4$ through various modification methods. Among them, element doping is the most common. For example, Zhang mixed tripoly cyanic acid with melamine phosphate and tripolythiocyanic acid to prepare phosphorus and sulfur-doped g-C$_3$N$_4$ porous nanospheres. Under visible light irradiation, sulfur-doped g-C$_3$N$_4$ hollow microspheres can achieve a hydrogen production rate of 22.3 μmol·h$^{-1}$, which is 13.2 times that of bulk g-C$_3$N$_4$ [26]. Yang mixed 500 mg dicyandiamide (DCDA) and 350 μL indium precursor solution (InCl$_3$) to prepare interlayer doped In-g-C$_3$N$_4$ catalysts by In-situ copolymerization, and then mixed 80 mg In-g-C$_3$N$_4$ with 25, 50 and 100 mg K$_2$HPO$_4$ respectively to obtain In, P-g-C$_3$N$_4$ catalysts. The optimal photocatalytic hydrogen production rate (4.03 mmol·h$^{-1}$·g$^{-1}$) is 50 times that of the original g-C$_3$N$_4$ (0.08 mmol·h$^{-1}$·g$^{-1}$) [27]. There are also scientific research teams that compound g-C$_3$N$_4$ with other materials to increase its specific surface area, thereby enhancing its light absorption efficiency. The construction of heterojunction can also greatly increase the hydrogen production rate. For example, Wang [23] prepared a double Z-type WS-WO/CNs heterojunction including CNs-WO and WS-WO Z-type structures with a hydrogen production rate higher than that of pure g-C$_3$N$_4$, which is about 57 times higher. In addition, some studies have successfully optimized the hydrogen production performance by preparing chain-like g-C$_3$N$_4$ to expose more active sites. Therefore, it is of great research value to enhance the photocatalytic hydrogen production performance of g-C$_3$N$_4$ by means of modification.

![Schematic Diagram of Hydrogen Production](image)

Figure 3 (a) Schematic Diagram of Photocatalytic Hydrogen Production from Sulfur-Doped g-C$_3$N$_4$ Prepared by Zhang [26]. (b) Schematic Diagram of the Configuration and Hydrogen Production Mechanism of In, P-g-C$_3$N$_4$ Prepared by Yang [27]. (c) Schematic Diagram of the Energy Band of WS-WO/CNs Prepared by Wang [23]. (d) The Photocatalytic Hydrogen Production Efficiency of Materials Modified by Various Researchers in Recent Years has Reached the Multiple of the Original Materials [22-23, 26-30]
3.2 Photocatalytic Degradation of Organic Pollutants

After absorbing visible light, g-C₃N₄ can produce strong oxidizing free radicals, and then organic pollutants can be oxidized and degraded through redox reaction. Therefore, g-C₃N₄ is also one of the hot topics for many researchers in the direction of degradation of organic pollutants. Through the modification process, the number of active free radicals can be increased, which enhances the oxidability and improves the degradation rate. Jiang used nitrogen self-doping and thermal exfoliation methods to adjust the surface characteristics and electronic structure of g-C₃N₄, so that its degradation rate for tetracycline hydrochloride (TC) was 76.78%, much higher than that of the original g-C₃N₄ (52.21%) [31]. Meng used in-situ acid-induced formation of tungstic acid-melamine hydrochloride precursors, and then obtained WO₃/g-C₃N₄ heterojunction photocatalysts with different morphologies by hydrothermal treatment and thermal condensation methods, which showed excellent photocatalytic activity in the degradation of pollutants paracetamol (APAP) and methyl p-hydroxybenzoate (MPB). After 30 minutes of visible light irradiation, the photocatalytic degradation efficiency of WO₃/g-C₃N₄ for APAP reached 98.2%, while the original g-C₃N₄ was only 30.1% [18]. E. Prabakaran et al. doped KF onto g-C₃N₄ by thermal method to form KF-g-C₃N₄. Under visible light irradiation for 100 minutes, the percentage of photocatalytic degradation of MB increased from 29% to 99% [32]. In addition, some research teams have broadened the range of light absorption through oxygen doping and loading Ag nanoparticles, thereby improving photocatalytic activity and degradation rate.

Photocatalytic technology can completely convert environmental pollutants into non-toxic small molecules at room temperature, which has almost no harm to the environment and greatly improves the efficiency of environmental restoration. Thus, it has broad application prospects in the degradation of organic pollutants.

Figure 4 (a) Band Structure of Nitrogen Self-Doped g-C₃N₄ Nanosheets Prepared by Jiang and the Schematic Diagram of Their Photocatalytic Degradation of TC [31]; (b) Band Structure of WO₃/g-C₃N₄ Prepared by Meng and the Schematic Diagram of the Z-Type Photo-Generated Carrier Transfer Mechanism [18]; (c) Mechanism of Photocatalysis of MB by KF-g-C₃N₄ Prepared by E. Prabakaran [32]; (d) Photocatalytic Degradation Rate of Materials Modified by Various Researchers in Recent Years has Reached the Multiple of the Original Material [16, 18, 24, 31-34]
3.3 Photocatalytic Antibacterial

The strong oxidizing radicals produced by g-C3N4 under light can be used to inactivate microorganisms. Meanwhile, g-C3N4 can be used as a carrier to disperse metal nanoparticles as antibacterial agents for materials, so it is also often used for antibacterial. For example, Huang reacted 1g g-C3N4 with 1mmol, 2mmol, 3mmol and 4mmol CuCl2·H2O respectively to prepare Cu/CN-C with different concentrations, and combined it with low melting point polyester (LMPET) fibers by dipping-hot bonding method, in which the antibacterial rate of 3Cu/CN-C@LMPET against Escherichia coli and Staphylococcus aureus (S. aureus) reached 99.00% and 99.80% respectively [35]. Umair Baig et al. used pulsed laser post-treatment technology to immobilize nickel oxide nanoparticles (nNiO) on the polymer surface of graphite carbonitride (g-C3N4) to synthesize n-NiO@g-C3N4 composite, with its MBC against Staphylococcus aureus and Pseudomonas aeruginosa only half that of pure g-C3N4 [36]. Zhang et al. prepared nanowire-rich super-hydrophilic g-C3N4 films by vapor-assisted closed deposition. This structure is conducive to the close contact between g-C3N4 and bacteria, which can effectively separate electrons and holes. Under visible light irradiation, the disinfection efficiency of nanowire-rich g-C3N4 films can reach more than 99.99% within 4 hours [37].

In recent years, water pollution has become more and more serious. Photocatalytic antibacterial technology can efficiently treat harmful pollutants and solve environmental problems, which has become an important application prospect in the field of environmental governance.

4. Conclusion

g-C3N4 is a new type of photocatalytic material with a special structure. Up to now, the methods commonly used to prepare g-C3N4 include solid phase synthesis, hydrothermal method, electrochemical deposition method and so on. The operation of electrochemical deposition is relatively simple and the requirements for equipment are not high, but there are many restrictions on the size and performance of the product. In contrast, the hydrothermal method has higher requirements for production equipment, but the performance of the product is also better. If you need to prepare g-C3N4 with special morphology, the best choice is the solid phase synthesis. However, g-C3N4 still has problems such as a small specific surface area and a high photo-generated electron-hole recombination rate, which can be improved by morphology regulation, element doping and semiconductor recombination. The modified g-C3N4 has been widely used in photocatalysis. For example, the modified g-C3N4 containing a double Z-type heterojunction structure can greatly improve the hydrogen production performance. The g-C3N4 compound with potassium salt has a larger surface area, smaller pore size and lower band gap energy, which has an excellent performance in the degradation of organic pollutants. In the field of antibacterial, thin-film g-C3N4 and its composites have shown better efficiency through closer contact with bacteria.

Due to the action of the aromatic C-N heterocycles and the strong van der Waals force between the layered structures, g-C3N4 also maintains chemical stability at high temperatures and in most strong acid and base solvents. Thanks to this advantage, g-C3N4 has a variety of preparation methods that meet different conditions. There are also effective modification methods in the fields of photocatalytic hydrogen production, degradation of organic pollutants, and antibacterial. Hence, g-C3N4 has a vital application prospect in various fields of photocatalysis research.

References


