

Research progress on Graphitic Carbon Nitride for the Removal of Sulfate from Mine Wastewater

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Abstract. Acid mine wastewater discharge is a serious environmental problem faced by the global mining industry. It has the traits of extensive contamination, protracted duration, and severe injury. How to effectively treat acidic mine wastewater is an important issue. Because of the rapid development of electrochemistry, many industries have used graphitic carbon nitride (or can be expressed as the chemical formula $g-C_3N_4$) to remove sulfate and metal ions from acidic mine wastewater. In this paper, the current research progress of graphitic carbon nitride is summarized, and the spatial structure of graphitic carbon nitride and its application in purifying mine wastewater are reviewed. Some fundamental facts about graphitic carbon nitride are introduced, along with its source and preparation. This paper mainly describes and analyzes the ways to modify graphitic carbon nitride (chemical modification, such as doping with a single element). It will assist in increasing the catalytic degradation capacity of $g-C_3N_4$ in the future and achieve better progress in environmental science by summarizing the pertinent research findings of $g-C_3N_4$ in the field of treating acidic mine wastewater.

Keywords: Graphitic carbon nitride, mine wastewater, chemical modification, single-element doping.

1. Introduction

The ecological environment and public health are constantly at risk from low-pH acid mine drainage (AMD), which, along with several heavy metals and sulfates, is discharged from coal mines [1]. Acid mine drainage (AMD) is a common byproduct of groundwater's long-term action, particularly in high-sulfur coal mines when extensive exposure to hematite and pyrite occurs. AMD is made up of sulfuric acid, iron (Fe^{2+} , Fe^{3+}), manganese (Mn^{2+}), and other metals [2,3]. To be more precise, Fe^{2+} can be further oxidized to Fe^{3+} in an acidic environment and hydrolyzed to generate $Fe(OH)_3$. Wastewater produced through this procedure has high sulfate and heavy metal ion concentrations. Without any improved treatment, the direct discharge of acidic mine water endangers both human life and the environment.

Chemical, physical-chemical, and biological techniques are used in traditional treatment procedures. The chemical technique, however, suffers from issues such as a significant volume of slag, pipeline scaling, and secondary contamination [4]. Ion exchange and membrane separation are examples of physical and chemical processes that have drawbacks such as being expensive and unsuitable for large-scale use. Sulfate-reducing bacteria are used in this approach, which has more stringent pH and temperature requirements.

A treatment method based on electrochemical principles is capacitive deionization. When electricity is applied to remove ions, adsorption of anions occurs while adsorption of cations occurs on the positive and negative electrodes, respectively [5]. Because of its straightforward design and lack of secondary contamination, this method is extensively employed in the desalination of saltwater and has a significant impact on the removal of SO_4^{2-} from my effluent. The choice and preparation of electrode materials are crucial for capacitive deionization because they have an impact on how well ions adsorb. Electrode materials include things like carbon aerogels, charcoal, metals, and graphene.

Graphite carbon nitride has many covalent bonds with a high concentration of nitrogen. Carbon and nitrogen atoms have undergone sp^2 hybridization [6]. Graphite carbon nitride possesses shorter lateral adsorption and intercalation pathways, and higher pseudo capacitance overall, with many

points and attachment sites for other modified materials. However, g-C₃N₄ is limited in the electrochemistry field because of its small specialized area surface area and poor conductivity.

Single-element doping has been proven to be a successful strategy in recent years. Some substances, like phosphorus, oxygen, boron, sulfur, etc., can substitute for C/N atoms in g-C₃N₄ without causing lattice deformation or nitrogen defects, increasing the number of active sites for capacitors [7].

In this article, the chemical modification of graphitic carbon nitride by adding ferrum, Ag-doped g-C₃N₄, boron doping, and V-doped graphitic carbon nitride, will be mainly introduced.

2. Properties and Structure of g-C₃N₄

2.1. Spatial Arrangement

The CN atoms in the typical polymer semiconductor g-C₃N₄ are sp² hybridized to create a highly delocalized conjugated system [8]. While the C atoms' orbitals provide the highest occupied molecular orbital of g-C₃N₄ (homoconjugation), the N atoms' orbitals produce the lowest vacant molecular orbital (lumoconjugation). About 2.7 eV is the prohibited bandwidth between atoms, which may absorb solar spectrum blue-violet light with a wavelength less than 475. [9] The semiconductor band edge location of graphitic carbon nitride is ideal for water photolysis to create hydrogen and oxygen and satisfies the thermodynamic conditions. As seen in Fig. 1, g-C₃N₄ has the planar, two-dimensional sheet framework and two basic structural units: the triazine ring (C₃N₃, left structure), and the 3-s-triazine ring (C₆N₇, right structure). The two-dimensional nanosheets are joined together by the van der Waals force.

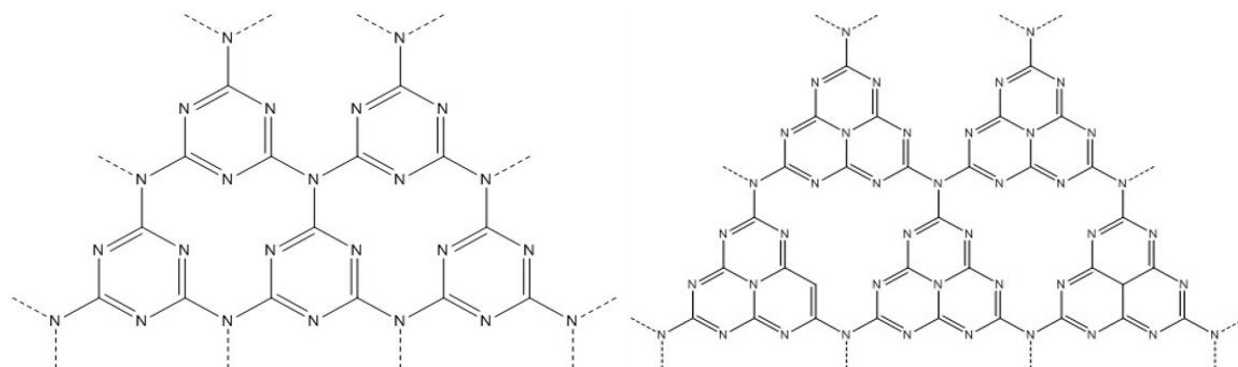


Figure 1. g-C₃N₄ molecular structure [9].

As a novel non-metallic photocatalytic substance, g-C₃N₄ can proceed with photocatalysis without the need for UV light due to its larger absorption spectrum. Additionally, g-C₃N₄ has strong chemical and thermal stability, with the thermal stability starting to deteriorate at temperatures beyond 600 degrees. Additionally, g-C₃N₄ can operate consistently in both strong acid and strong alkali environments, which is why this substance is used to clean acidic mining effluent.

2.2. Preparation of g-C₃N₄

g-C₃N₄ is not too difficult to prepare. With a short process flow, little equipment, minimal equipment needs, and quick preparation times, g-C₃N₄ may be made from a range of nitrogen-rich precursors (including dicyandiamide, urea, etc.) and preparation procedures. However, it is often made in a limited quantity at the laboratory level because of issues including low yield and low stability of completed goods, although some businesses have accomplished mass manufacturing. For example, there are three key stages for the synthesis of g-C₃N₄@L-arginine. Melamine can be first transformed into bulk g-C₃N₄, and then this substance is processed with liquid exfoliation and sonication to produce g-C₃N₄ nanosheets. Then, graphitic carbon nitride nanosheets were exposed to 1,3-dibromopropane for 24 hours in an environment of 100 degrees while being contained in an

atmosphere full of nitrogen. In the last stage, combining L-arginine and modifying g-C₃N₄ nanosheets can produce g-C₃N₄@L-arginine [10].

3. Chemical Modification of Graphitic Carbon Nitride

3.1. Ferrum Doping

Doping transition metals including Ag, Pb, Fe, Zn, and Ni into the graphite-like carbon nitride structure of g-C₃N₄ can improve its photocatalytic ability. The research discovered that iron elements like Fe₂O₃, FeCl₃, etc. are doped with g-C₃N₄ to create a composite photocatalyst that performs two kinds of catalytic degradation: photocatalytic oxidation and Fenton-type oxidation. A two-stage calcination thermal stripping technique and hydrothermal reaction may be used to combine iron-doped graphite carbon nitride. Analysis techniques used on the created composite materials included X-ray photoelectron spectroscopy, photoluminescence spectroscopy, etc. The composite material's specific surface area greatly increased. The main peak of iron can be seen in the X-ray photoelectron spectrum analysis at 706.7 eV, which is specifically divided into three different peaks (706.7, 709.3, and 724.0 eV), relating to the bond energies of Fe-N, FeO, and Fe₂O₃, respectively. This shows that the Fe-g-C₃N₄ Fe primarily exists in the form of Fe-N coordination bonds, which is helpful for the quick transfer and migration of photo charges between Fe₃. Because of this change, g-C₃N₄ breaks down and eliminates sulfate using its increased ion adsorption ability [11].

3.2. g-Doping

Noble metal (Ag) doped g-C₃N₄ photocatalysts may be created using the surface thermal condensation method. In addition to reducing the gap energy between atoms (the energy difference between the conduction band and valence band) and overall particle size, it has been discovered through N₂ adsorption-desorption tests that Ag doping may also improve the composition and distribution of surface elements in synthetic materials. It lessens electron/hole recombination and carrier separation in the structure of graphitic carbon nitride. Through this synthesis, removing sulfate from mine effluent may be hastened significantly [12].

3.3. Boron Doping

Melamine and boric acid can be used as starting ingredients to modify g-C₃N₄. B-doped graphitic carbon nitride electrode materials can be produced by examining the optimal addition ratio of boric acid doping. The amount of space accessible and the pore size in g-C₃N₄ are increased by a series of high-temperature boric acid reactions. The limitations of pure g-C₃N₄, such as poor conductivity, are improved by this chemical alteration. The rate at which SO₄²⁻ is removed from mine effluent may be significantly increased by using this capacitive deionization method. In theory, B-doping can substitute for C and N atoms to create lattice deformation and nitrogen defects. In the tris-triazine, boron doping mostly swaps out the C atoms. C-N bonds are broken during this process, and B-N bonds are created. This modification can enhance the material's electrosorption and electrode transfer capabilities without destroying the g-C₃N₄'s original framework structure. To treat SO₄²⁻ ions in mine wastewater, g-C₃N₄ will function better as a capacitive deionization (CDI) electrode material when doped with B. The highest electrosorption capacity (SEC) of the electrode after optimization was 14.70 mg/g when 30% boric acid was added. The removal rate of SO₄²⁻ from mine wastewater attained 75.4% after the CDI system had been operating for a while [13].

3.4. V-Doping

Poor responsiveness to visible light, poor charge separation efficiency, and little surface area are the primary drawbacks of g-C₃N₄. To create g-C₃N₄ with high catalytic performance, doping heteroatoms into the framework carbon has emerged as a major technique. The Vanadium (V) element may be a viable dopant to enhance the catalytic ability of g-C₃N₄ because of the same atomic

sizes. Thermal polymerization can be used to create g-C₃N₄ that has been doped with V. X-ray diffraction (XRD) analysis reveals that graphitic carbon nitride exhibits two peaks at 12.8 and 27.6 degrees distinctively. In g-C₃N₄ that has been doped with V, it is possible to see the peak connected to the (0 0 2) face, but no peak for V oxide was discovered. Pure g-C₃N₄ only eliminated 24.7% of the other contaminants (similar to the pollutants in mine wastewater) when they were chosen for investigation, demonstrating that the catalytic capacity of g-C₃N₄ was relatively poor. The V-doped g-C₃N₄ sample has a rather strong catalytic activity and may remove up to 40%. Thus, it is feasible to successfully integrate vanadium atoms into the original graphitic carbon structure, which greatly improves the separation of charges and intensifies the absorption of visible light, boosting the efficiency of sulfate pollutant degradation [14].

4. Applications and Prospects for Treatment of Mine in Wastewater

g-C₃N₄ and its derivative compounds are often used in a variety of sectors, including energy storage, catalysis, sensing, and adsorption [15] because of their sizable specific surface area, high thermal stability, and chemical inertness. Each year, significant amounts of poisonous heavy metal ions (including As, Pb, Cu, etc.) are released into the environment by industries like chemical production, mining, and battery manufacture, seriously harming the ecosystem. Using the mining sector as an example, mine effluent has a significant negative effect on both human health and the environment, with sulfate pollutants making up the majority of the pollutants. Sulfate may react with a variety of metal ions to create stable sulfate salts. The principal source of sulfate in water is the sulfate of formation minerals, namely calcium sulfate and magnesium sulfate. The destruction of soil structure decreased soil fertility, and corrosion of the water delivery system are the major effects of this pollution on the ecosystem. The g-C₃N₄ material has a reasonably large specific surface area, a good porous structure, and great dispersion. The material's surface edge also features a lot of N atoms with strong electron-attracting properties as well as a lot of -NH- and -NH₂ basic groups. All of these characteristics help g-C₃N₄ remove heavy metal ions from water efficiently [15]. The main interactions between g-C₃N₄-based materials and heavy metals occur through surface coordination, ion exchange, and electrostatic contact. The interaction between g-C₃N₄-based materials and organic matter is mainly governed by Lewis acid-base interactions, electrostatic interactions, and π -interactions. Numerous studies have shown how effective g-C₃N₄-based materials may be as adsorbents in the purification of water. Traditional treatment methods create enormous amounts of sludge, incur substantial treatment costs, are difficult to use, and have subpar results. Utilizing graphite materials provides minimal initial outlay, low ongoing expenditures, and is simple to utilize. It is particularly well suited to widespread application in the mining sector, where high input costs make it necessary to decrease resource consumption when treating wastewater and increase purifying effectiveness.

5. Summary

Mine wastewater brings huge harm to people and the environment. If the mine wastewater is not purified thoroughly enough, residual sulfate substances will remain in the water. Once people drink it, it may cause diarrhea and pain, and in severe cases, other physiological diseases. For the environment, acid mine wastewater can cause soil acidification and structural damage, thereby affecting the growth of plants and crops. Continuous developments in electrochemistry and materials science allow the use of catalyst materials to solve water pollution problems. g-C₃N₄ is a very promising chemical material that can decompose sulfates in mine wastewater by adsorbing metal ions. g-C₃N₄ is now mainly derived from experimental synthesis. By selecting appropriate carbon and nitrogen sources, g-C₃N₄ can be obtained under certain reaction conditions. Nevertheless, the actual application impact of g-C₃N₄ is severely constrained by issues with very quick electron-hole recombination, poor quantum efficiency, and inadequate specific surface area. Therefore, diverse energy band structures, electrical characteristics, and surface areas of g-C₃N₄ materials may be

efficiently regulated using a variety of improvement approaches, such as nano-modification, chemical doping modification, physical composite modification, etc. In this article, the chemical modification of graphite carbon nitride, including the doping of non-metal elements (B) and metal elements (Fe, Ag, and V), is mostly discussed. It describes how these adjustments enhance the impact of g-C₃N₄ on adsorption capacity. In this way, it is anticipated that g-C₃N₄ will get more attention in the future, play a bigger part in the field of treating water contaminants, and maybe even develop to filter additional home or industrial wastewater.

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