Academic Journal of Science and Technology
ISSN: 2771-3032 | Vol. 8, No. 1, 2023

Comparison of Modification Methods of Photocatalyst G-C3N4 in Hydrogen Production Performance

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Abstract: Non-metallic polymer semiconductor graphite phase carbon nitride (g-C3N4) is a low-cost, environmentally friendly raw material with suitable bandgap width and stable chemical properties. However, there are still problems such as lower surface area, higher recombination rate of photo-excited charge carriers, and lower utilization rate of visible light. This paper introduces the structure, physicochemical properties, preparation methods, and modification ideas of graphite phase carbon nitride, focusing on several popular modification achievements in recent years, as well as a horizontal comparison of their respective production methods, mechanisms, and hydrogen production efficiency. Finally, the challenges and prospects in the modification of carbon nitride are discussed.

Keywords: Graphite phase carbon nitride, Solar energy, Hydrogen production, Structural modification, Photocatalyst.

1. Introduction

Energy is an important support for human development and the foundation of modern social development. Its importance to the economy, society, and environment of modern society is self-evident. With the vigorous development of productivity in various countries, the consumption of fossil fuels is increasingly increasing, and the problem of energy shortage is gradually emerging. With the combustion of fossil fuels, related environmental problems have also quietly emerged. The threat to human survival from environmental issues such as global warming and haze is also increasing. As one of the world's largest carbon emitting countries and a major power, China has fulfilled its corresponding responsibilities to address climate change and reduce carbon emissions. In September 2020, China clearly set the goals of " peak carbon dioxide emissions" and "carbon neutrality" by 2030. In the context of carbon neutrality strategy, the use of new energy and changing the energy structure will become a major trend in the future, and the development of environmentally friendly, efficient, renewable, convenient storage, and sustainable green energy hydrogen energy is extremely important. One of the most ideal ways to solve the global energy shortage and environmental damage is to use solar energy to decompose water to produce hydrogen energy. The key point of this technology is how to develop environmentally friendly, efficient, and low-cost photocatalysts. Previously, catalysts used for water decomposition were precious metal catalysts, such as platinum and palladium metals. The non-metallic polymer semiconductor graphite nitride carbon (g-C_3N_4) has a two-dimensional layered structure similar to graphite stacking, and has a highly delocalized Π conjugated system formed by sp^2 hybrid carbon and nitrogen atoms. Compared with traditional precious metals, it has the advantage of low cost and it also has advantages such as suitable band positions (suitable bands are used for water oxidation and proton reduction), safety and stability. In summary, non-metallic polymer semiconductor graphite phase carbon nitride (g-C_3N_4) is a photocatalyst that can have a profound impact on future prospects.

Research has shown that g-C_3N_4 has problems such as low surface area, high photo excited carrier recombination rate, and low visible light utilization, resulting in low photocatalytic hydrogen production efficiency. To address the above issues, scientists have proposed various modification methods with different schemes to compensate for the adverse effects caused by these shortcomings. The commonly used methods to improve g-C_3N_4 photocatalytic decomposition of water for hydrogen production include morphology control, co-catalyst loading and semiconductor alignment, and heteroatom doping. Reasonable structural design can not only improve the intrinsic properties of g-C_3N_4, but also greatly enhance its performance in photocatalytic hydrogen production.

2. Principle

2.1. The structure and properties of g-C_3N_4

Graphite type carbon nitride has special physical and chemical properties due to its unique structure. It has a two-dimensional layered structure similar to graphite stacking, and has a highly delocalized Π conjugated system formed by sp^2 hybrid carbon and nitrogen atoms. The van der Waals force between layers makes it have good thermal and chemical stability. According to research, graphite type carbon nitride can maintain its stability and does not decompose when heated to 600 degrees Celsius (exposed to air), and it is not easily soluble in common solvents such as water, ethanol, acetone, etc. And graphite type carbon nitride also exhibits strong acid and alkali resistance, which can maintain its stability in hydrochloric acid solution with a pH value of 1 and sodium hydroxide solution with a pH value of 14.

And graphite type carbon nitride is also an excellent organic semiconductor material that can exhibit good photoelectric properties. On the research surface, the absorption cutoff wavelength of graphite type carbon nitride solid for ultraviolet visible light is approximately 420 millimeters, with a corresponding bandwidth of 2.7 eV (the results may be affected by different experimental conditions). Graphite type carbon nitride can emit blue fluorescence, with a fluorescence peak at 470nm and a lifespan of 1-5ns. This characteristic makes graphite type carbon nitride a new type of solar energy conversion material. From the figure, it can be seen that the valence band and conduction band of graphite type carbon nitride contain the oxidation-reduction potential of water. Therefore, in theory, graphite type carbon nitride can both oxidize water to obtain oxygen and reduce water to hydrogen gas.

2.2. Basic principle of photocatalytic water splitting reaction

The energy band structure of semiconductor catalysts is different from that of metal catalysts. The energy band of metal catalysts is due to the different attraction of metal atoms at different distances on lattice nodes to valence electrons, leading to the splitting of electronic energy levels, resulting in smaller energy level differences and gradually denser energy levels, ultimately forming energy bands. The band structure of semiconductor catalysts is discontinuous, with atoms and molecules present in the semiconductor crystal. Due to the interaction between atoms and molecules, their highest occupied orbitals form valence bands, while their lowest empty orbitals form conduction bands. Electrons can move freely between the valence and conduction bands, and there is a region between the valence and conduction bands where electrons can’t move to become a bandgap. The size of the bandgap region is called bandgap energy (Eg).

In the process of photocatalytic decomposition, the conduction band transitions, and photogenerated electrons e- is generated on the conduction band. The corresponding number of photogenerated holes h+ are left on the valence band, creating electron hole pairs inside the semiconductor photocatalyst. Therefore, the conduction band is reducible and the valence band is oxidizing. The generated photogenerated electrons and holes will be transferred to the surface of the semiconductor photocatalyst, and the photogenerated electrons that migrate to the surface of the semiconductor material will reduce H+ to form hydrogen gas. The photogenerated holes will oxidize the sacrificial agent, and of course, the photogenerated electrons and holes will also recombine, reducing the number of electrons and holes used in the reaction.

2.3. Preparation Method of Graphite Carbon Nitride

The precursors of g-C3N4 are compounds rich in nitrogen and containing C-N structures. Common synthesis methods include electrochemical deposition, solvothermal method, solid-state reaction method, and thermal condensation polymerization method.

2.3.1. Electrochemical deposition method

Place the precursor on a silicon or other substrate, supplemented by high-voltage electricity, and react for a certain time to obtain g-C3N4. Li and others used saturated acetonitrile with cyanuric acid chloride and melamine to obtain g-C3N4 thin films.[1]

2.3.2. Solvothermal method

Using organic solvents or non-aqueous solvents as the reaction medium, precursor is added and placed in a special sealed container such as a high-pressure kettle at a certain temperature and pressure. After a period of reaction, g-C3N4 can be obtained.

2.3.3. Solid-state reaction method

Preparation of g-C3N4 using melamine or cyanuric chloride with triazine structure and the chemical reaction between solids to produce a new solid**.**

2.4. Several ideas of modification

2.4.1. Morphological control

Due to the fact that the structure of g-C3N4 is a two-dimensional layered material similar to graphite, consisting of a large number of stacked layers, this compact structure places it in a bulk structure, which greatly limits the specific surface area of g-C3N4. Therefore, we can adjust its morphology and prepare g-C3N4 into nanostructures, or hollow or porous structures to increase the specific surface area [2].

Papailias and others undergo glass treatment on g-C3N4 prepared from melamine through chemical stripping and hot glass [3]. The specific surface area of bulk g-C3N4 obtained from chemical glass is as high as 9.64m2/g, while the specific surface area of chemically peeled g-C3N4 is even as high as 134.42m2/g, demonstrating excellent NOX oxidation ability under visible light.

2.4.2. Co-catalyst loading and semiconductor recombination

The commonly used co-catalysts for modifying g-C3N4 include precious metals (such as platinum, gold, etc.), inexpensive metals (such as metal sulfides, metal phosphides, etc.), and some carbon materials (such as graphene quantum dots). These materials can form Schottky energy barriers with g-C3N4, forming heterojunctions and reducing the recombination rate of photo generated carriers, and thus improve photocatalytic performance [4].

2.4.3. Heteroatom doping

The van der Waals force between g-C3N4 layers is weak and the layers are composed of covalent bonds, so g-C3N4 can be easily modified by doping other substances. Commonly used include non-metallic element doping, mental element doping, and organic molecule doping.

(1) Doping of non-metallic elements

G-C3N4 can be co-doped with transition metals (such as Fe, Co, etc.) and non-metallic elements (such as S, B, etc.) to effectively change the structure of g-C3N4. Bhagat et al. co loaded Co and B onto g-C3N4, where B made g-C3N4 a p-type semiconductor and Co made g-C3N4 an n-type semiconductor [5]. Both of them had partial charge compensation, which reduced the recombination rate of photo generated holes and electrons, changed the potential value, and improved photocatalytic performance.

(2) Metal element doping

Doping g-C3N4 with transition metals (such as Fe, Co, etc.) and alkali metals (such as Na, K, etc.) can use metals as capture sites for charge carriers, improve electron mobility, and accelerate the separation rate of photo generated charge carriers. Gao et al. used a simple one-step pyrolysis process to incorporate Fe into g-C3N4 nanosheets, accelerating electron transport speed and increasing specific surface area, thereby enhancing photocatalytic properties [6].

(3) Organic molecule doping

The doping of organic molecules can expand the Π conjugation system of g-C3N4 to a certain extent, accelerate the migration and separation of photo generated electrons and holes, and enhance the photocatalytic performance. Guo et al. coupled PNA (nitrobenzoic acid) to g-C3N4, which narrowed the band gap of g-C3N4, absorbed more solar energy, and introduced gradients in the electron potential distribution on the surface of the photocatalyst [7].

3. Application of Carbon Nitride

3.1. Photocatalytic degradation of organic pollutants

Using photocatalysts to degrade pollutants is a clean and efficient treatment method, which utilizes the special structure of photocatalysts to generate photo generated charge carriers under sunlight. Photogenerated charge carriers can form · OH, · O2- and other substances with external particles on the semiconductor surface, degrading VOCs adsorbed on the semiconductor surface into CO2 and H2O, thereby achieving deep purification of VOCs. For example, Yan et al. found through comparative experiments that the photodegradation mechanism of two typical dyes[8], Rhodamine B (Rh B) and methyl orange (MO), is based on the oxidation of photo generated holes in g-C3N4, while methyl orange (MO) relies on the reduction of photo generated electrons in g-C3N4.

3.2. Water splitting

Using sunlight to decompose water to produce H2 is one of the most ideal methods for producing hydrogen energy, which can solve the ecological, energy and other problems faced by humans, so it is extremely important to choose and develop the most suitable catalyst for decomposing water. Many metal oxides have such functions. In 2009, Wang et al. first validated the functionality of g-C3N4 as a semiconductor material for photocatalytic water decomposition, without relying on complex device manufacturing [9]. This result represents that in the study of photocatalysis, artificially conjugated polymer semiconductors can be used as energy transducers.

4. Summary of Latest Research Modification Methods

Table 1. Summarize 16 modification methods for g-C3N4

Number	Method	Required Materials	Hydrogen production efficiency
1	MoS2 and Fe2O3 co-modify g-C3N4	Na2MoO4·2H2O,1.56 g L-cysteine,CN,Fe(NO3)3·9H2O ,(NH4)2CO3 (0.5 M)	Precipitation amount of H_2 is 7.82 mmol·g^{-1} h^{-1}
2	ZnOFe2O3 co-modify g-C3N4	Melamine, Zinc nitrate , Non hydrated iron nitrate, ethanol	Precipitation amount of H_2 is 25 μmol·h−1,activityis 6.5 μmol·$g^{-1}h^{-1}$
3	Bio-inspired Z-scheme gC3N4 Ag2CrO4	Urea, Ultrapure Water, K2CrO4, AgNO3 , ethanol	Activity is 902.1 μmol g−1h−1
4	electron transfer over Ni- and Co -sulfde co-doped g-C3N4	Melamine, Ultrapure Water,CoSO4•7H2O Ni(NO3)2•6H2O,Na2S•9H2O, ethanol	Hydrogen evolution rate is 100μmol/h
5	Ag/AgBr/g-C3N4	Urea, ethanol,AgNO3,[Amim]Br solution	Activity is 587.6μmol $g^{-1}h^{-1}$
6	MnFe2O4@g-C3N4	Citric acid, Fe (NO3)3·9H2O, Mn (NO3)3·6H2O,g-C3N4	Hydrogen evolution rate is 3200μmol/L
7	Eu doped g-C3N4	europium,g-C3N4	Activity is 128.8 mmol•g−1•h−1
8	Ball-milled Ni2P/g-C3N4	EDA,Ni(H2PO2)2·6H2O ,NaH2PO2,NaBH4, Melamine	128.7 mmol•g−1•h−1
9	g-C3N4-Au/Ni3(VO4)2	Melamine,Ni(NO3)3·0.5H2O , nitric acid,NH4VO3,NaOH	Activity is 3345μmol·h−1 g−1
10	Bi2O2CO3/g-C3N4@PAN nanofibers	g-C3N4,PAN,DMF Bi(NO3)3 · 5H2O(99.9%) , Urea, deionized water,CB	Activity is 5396mmol•g−1•h−1
11	Layered TiO2 spheres modified g-C3N4 nanocomposites	Melamine, urea, ethanol, nitric acid, TiCl4, dilute ammonium sulfate	Activity is 286 mmol·h−1·g−1

5. Conclusion

This article introduces 16 modification methods of graphite phase carbon nitride, providing ideas for designing g-C3N4 composite photocatalysts with low photo generated carrier recombination rate, special structure suitable for absorbing light, and high photocatalytic efficiency. There are still many methods and materials with great application potential waiting for us to explore and research.

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