g-C\textsubscript{3}N\textsubscript{4} Photocatalysis Technology Application in Water Treatment

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Abstract: Photocatalytic oxidation is a green environmental protection technology which collects sewage for advanced treatment environmental protection and saves water resources. It is praised as the most promising advanced oxidation technology for environmental purification in the 21st century. The reaction mechanism of g-C\textsubscript{3}N\textsubscript{4} photocatalytic treatment was reviewed, the main research directions of g-C\textsubscript{3}N\textsubscript{4} photocatalyst and its modification were briefly analyzed, and the research and application of g-C\textsubscript{3}N\textsubscript{4} photocatalysis technology in water treatment were discussed. Finally, the future photocatalytic technology of g-C\textsubscript{3}N\textsubscript{4} is prospected, and it is hoped that it will be helpful to the work in related fields.

1. Introduction
With the intensification of water pollution and the improvement of water quality standards, the complexity of water pollution is becoming more and more serious. The reuse of wastewater after advanced treatment is one of the most effective means to alleviate the current water shortage. At the same time, the study of photocatalytic properties of semiconductor based on the background of solar chemical conversion and storage began in 1917. However, until 1972, the "Bendo Fujima effect[1]" was obtained, which marks the beginning of a new era of heterogeneous photocatalysis. Photocatalytic technology can remove pollutants from water at room temperature and atmospheric pressure by using cheap solar energy without secondary pollution[2]. In recent years, photocatalytic technology has developed into an ideal environmental treatment technology[3]. The main factors affecting photocatalytic efficiency are semiconductor band gap, morphology, carrier separation and migration efficiency[4]. Since ultraviolet light accounts for less than 5% of solar light and visible light is 48%, the core of photocatalysis is the development of efficient, stable and inexpensive visible light responsive photocatalysts. Graphite phase carbon nitride g-C\textsubscript{3}N\textsubscript{4} is a new type of nonmetallic semiconductor photocatalyst, which consists only of C and N elements, which makes it have obvious advantages over other metal photocatalysts, and the band gap of this material is narrow (2.7eV), good stability, easy structure and performance Regulation is a promising visible light catalyst, widely used in organic synthesis, photodegradation of organic pollutants, photolysis water for hydrogen production and other reactions [5,6]. At present, g-C\textsubscript{3}N\textsubscript{4} photocatalyst has become a hot research topic in the field of environment and energy science, which requires researchers to further improve and develop the application of g-C\textsubscript{3}N\textsubscript{4} photocatalytic oxidation technology in water treatment.

2. Photocatalytic treatment mechanism
Photocatalysis is an advanced oxidation technique that uses semiconductor materials as catalysts. When
light with energy equal to the band gap of semiconductors is irradiated onto the surface of the catalyst, electrons in the semiconductor will be excited to move from valence band to conduction band. A highly active electron-hole pair is formed, which reacts with the surface of semiconductors, such as dissolved oxygen, water molecules, and so on, resulting in highly oxidized "HO·", and then through the addition, substitution, and electron transfer between "HO·" and pollutants. Make the contaminants completely or partially mineralized, and finally achieve the purpose of degrading the contaminants [7].

The semiconductor photocatalytic reaction can be divided into three steps according to the traditional theory[8]: first, the generation of carriers, the valence band electrons are excited by the light quantum into the conduction band, a positively charged hole is formed on the valence band. The electron and hole carriers have the ability to reduce and oxidize the intensity corresponding to the band gap, followed by the transport process of the carriers, and some of the photogenerated carriers will collide with each other. Defects and other causes occur in the semiconductor internal recombination, while the other part of the longer life, higher mobility will migrate to the surface; ultimately, carrier participation in the reaction process, migration to the surface of the semiconductor active space Holes interact with electrons and substances in the environment to complete the photocatalytic process.

3. Ways to improve the activity of semiconductor photocatalyst

3.1. Nonmetallic modification
Nonmetallic elements that modify g-C₃N₄ include S, C, B, F, N, P, O and other elements. It is generally believed that these nonmetallic elements replace Con NH element in 3-striazine structural unit, which makes g-C₃N₄ form character defect, which leads to the effective separation of photogenerated electrons from hole pairs. Thus, the photocatalytic activity was improved effectively. Table 1 summarizes the preparation and properties of g-C₃N₄ doped nonmetallic elements in recent years. Cui Yumin et al.[9] prepared CNI catalyst using dicyandiamine and amine iodide as raw materials, and then mixed CNI and SiO₂ with water bath method. The composite photocatalyst SiO₂/CNI was prepared by calcination. Under the optimized conditions, the photocatalytic decomposition rate of aquatic hydrogen by SiO₂/CNI reached 88.6µmol/h. The photocatalytic activity of g-C₃N₄ can be improved by expanding the response of g-C₃N₄ in the visible region and increasing the photocatalytic activity.

3.2. Precious metal deposit
The mechanism of doping is that the doped elements can generate donor energy levels above the valence band or the acceptor energy levels below the conduction band. After the semiconductor absorbs the energy of the photon, it excites the electrons from the valence band to the conduction band. The electrons are also excited from the donor level to the conduction band or from the valence band to the acceptor level, which makes the band gap of g-C₃N₄ narrow and the absorption range enlarged. It is found that
the noble metal can be modified on the surface of g-C3N4 catalyst by depositing it on the surface of g-C3N4 catalyst. Table 2 summarizes the preparation and properties of g-C3N4 doped metal elements in recent years.

| PRECURSOR    | mix element | Photocatalytic performance (compared with pure G-C3N4) |
|--------------|-------------|------------------------------------------------------|
| CYANOGLYAN DINE | K           | Degradation of phenol and RhB by 3.3 and 4.8 times [16] |
| CYANOGLYAN DINE | Ag          | Degradation of MB by 0.7 times [17] |
| MELAMINE     | Fe          | Degradation of RhB increased by 0.45 times [18] |
| CYANAMIDE    | Pd          | Enhanced efficiency in the degradation of bisphenol A [19] |
| CYANAMIDE    | Pt          | Increase in hydrogen production efficiency by 10 times [20] |
| CYANOGLYAN DINE | Zn          | Increase in hydrogen production efficiency by 10 times [21] |

3.3 Recombination of g-C3N4 with other semiconductors

Due to g-C3N4 is a polymer with low crystallinity and high exciton binding energy, it is unfavorable to the separation and migration of photogenerated carriers, which leads to lower quantum efficiency of photocatalysis. By combining g-C3N4 with other semiconductor materials, the photogenerated carriers can be separated from each other in space, which can inhibit the recombination of carriers and improve the photocatalytic performance. Fettkenhauer et al.[22] developed a SnO2/g-C3N4 composite photocatalyst. Under visible light irradiation, the hydrogen production efficiency of g-C3N4 was improved. Kumar et al.[23] synthesized N-doped ZnO/g-C3N4 core-shell catalyst( N/ZnO/g-C3N4 ) for the degradation of RhB in visible light, which is higher than that of single-phase g-C3N4 or N-doped ZnO catalyst. Zhang et al.[24] synthesized CdS/g-C3N4 photocatalyst, the valence band of CdS is 1.9eV, the conduction band is -0.5eV, and the valence band of g-C3N4 is higher than that of CdS, while the valence band of g-C3N4 is lower than that of CdS, so that the electrons in the conduction band are injected into CdS from g-C3N4, and the hole flows to g-C3N4, which makes photogenerated electron hole pairs separate in space. Their synergistic effect also makes their catalytic effect better than that of single CdS or g-C3N4.

4. Application of photocatalytic technology in water treatment

4.1 Photocatalytic degradation of pollutants

Photocatalytic degradation of pollutants is a clean and efficient method for the treatment of organic pollutants, and the degradation of many pollutants under visible light is a hot and difficult point in the field of photocatalysis. Pei Zhaojun et al.[25] used melamine as the reaction precursor, the graphite phase carbonated nitrogen obtained by microwave-assisted sintering has the better ability of photocatalytic degradation of Rhodamine B wastewater by visible light, and the decolorization reaction is relatively rapid and no secondary pollution. Compared with other treatment technologies, this method has the advantages of low cost, stable catalytic performance and more convenient operation. Huang Liying et al.[26] synthesized g-C3N4/MoO3 composite photocatalytic materials by ultrasonic dispersion heat treatment. The results of visible photocatalytic degradation of methylene blue showed that the photocatalytic degradation accorded with the first-order reaction kinetics. Among them, 7% composite has the highest photocatalytic activity, the degradation rate is 93% after illumination, and the degradation rate constant is 4.2 times of g-C3N4 and 1.9 times of MoO3 respectively. The unique electronic structure and physicochemical properties of g-C3N4 make it suitable for photocatalytic degradation of many
organic pollutants, including RhB, MO, MB, bisphenol A, benzyl alcohol, tetracycline hydrochloride et al. g-C₃N₄ can also be used to remove NO and reduce heavy metal Cr (VI) in air.

4.2 Photocatalytic decomposition of Aquatic hydrogen
Decomposing water under visible light to produce hydrogen and converting solar energy directly into hydrogen energy is one of the ideal ways to solve the problems of energy and environment faced by human beings. Theoretically, due to the valence band and conduction band of g-C₃N₄ are in the proper position, the photoreduction of water to produce hydrogen and oxidation to produce oxygen can be carried out. However, the photocatalytic decomposition of water under visible light is still difficult and rarely reported. This is because the oxygen-producing reaction is a four-electron complex reaction which is more difficult than the hydrogen-producing reaction.

In recent years, g-C₃N₄ has been widely used in hydrogen production as a photocatalyst. However, the photocatalytic activity of pure g-C₃N₄ is not high, so it needs to be modified, including the preparation of porous g-C₃N₄, elemental doping, molecular doping, composite carbon materials and so on. It should be noted that the photocatalytic production of hydrogen with g-C₃N₄ requires coupling and suitable cocatalyst, mainly including precious metal (Pt, Au, Ag, et al.) and non-precious metal (NiS, NiS₂, MoS₂, WC, et al.).

4.3 Photocatalytic reduction of CO₂
In addition to photocatalytic hydrogen production, photocatalytic reduction of CO₂ to produce hydrocarbon fuels is one of the means to solve the problem of energy. Recent studies have shown that g-C₃N₄ can be used as a potential photocatalyst for reducing CO₂. The ability of g-C₃N₄ ( u-g-C₃N₄ ) to reduce CO₂ as a potential reduction CO₂ is stronger than that of g-C₃N₄ ( m-g-C₃N₄ ) prepared by using melamine as a precursor, and the reduction product is CH₃OH and C₂H₅OH, while the reduction product of m-g-C₃N₄ is only C₂H₅OH. The recombination of g-C₃N₄ with other semiconductors can effectively improve the activity of photocatalytic reduction of CO₂ by g-C₃N₄. CAO et al.[28] found that semiconductor heterostructures such as g-C₃N₄/In₂O₃ could photocatalyze the reduction of CO₂ to CH₄, thus turning CO₂ into a directly usable fuel. However, the research on photocatalytic reduction of CO₂ is still few, and the photocatalyst is unstable, so it still needs to be explored for a long time.

5. Conclusion
As a new type of non-metallic photocatalyst, graphite phase carbon nitride has unique electronic structure and suitable valence band position, and also has the advantages of high thermal and chemical stability, low price and environmental protection, etc. In recent years, the report of photocatalytic reaction has been increasing rapidly, and has a broad application prospect in the field of environmental engineering, and has become a new research hotspot. However, the modification of g-C₃N₄ with other photocatalytic materials still has many key scientific and technological problems, which will limit its popularization and application, which can be further explored from the following aspects:

(1) Furthermore, various technical methods were adopted to modify g-C₃N₄ photocatalyst. For example, the combination of nanostructure control and copolymerization method can not only optimize the chemical composition of catalytic materials and control their energy band structure, but also control the surface morphology and nanostructure of catalytic materials, and improve the activity of various photocatalytic reactions.

(2) The photocatalytic mechanism of g-C₃N₄ was studied. Only by understanding the photocatalytic mechanism of g-C₃N₄ theoretically can the photocatalytic activity of g-C₃N₄ be improved.

(3) Further explore the Application of g-C₃N₄ photocatalytic Oxidation Technology, such as removal of Organic pollutants under anaerobic conditions.

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References

[1] Fujishima A and Honda K 1972 Electrochemical Photolysis of Water at a Semiconductor Electrode J. Nature 238 37-38

[2] Guiying L, Xin N, Yanpeng G and Taicheng A 2016 Can environmental pharmaceuticals be photocatalytically degraded and completely mineralized in water using g-C3N4/TiO2 under visible light irradiation? J. Applied Catalysis B Environmental 180 726-32

[3] Hui Z, Lixia Z, Fanglan G and Lianghong G 2016 Carbon Dots Decorated Graphitic Carbon Nitride as an Efficient Metal-free Photocatalyst for Phenol Degradation J. Applied Catalysis B Environmental 180 656-62

[4] Chuyong Z, Bo Yang Yannan Y 2014 Progress in photocatalytic activity of g-C3N4 J. Journal of inorganic materials 29 785-94

[5] Fenfen L and Yongfa Z 2016 Enhancement of mineralization ability for phenol via synergetic effect of photoelectrocatalysis of g-C3N4 film J. Applied Catalysis B Environmental 180 324-29

[6] Yukai Z, Ruiren T and Rong H 2015 Palladium Supported on Graphitic Carbon Nitride: An Efficient and Recyclable Heterogeneous Catalyst for Reduction of Nitroarenes and Suzuki Coupling Reaction J. Catalysis Letters 145 1961-71

[7] Guoning C, Xingquan L and Xiaohuo Z 2008 Progress in photocatalytic treatment of Papermaking Wastewater J. Chinese Journal of Papermaking 23 101-05

[8] Qu Y 2018 The way to a better World—photocatalytic Technology J. New energy trade and trade observation 03 92-94

[9] Yuming C, Ruijuan S, Huiquan L and Hui T 2016 Preparation of SiO2/CNI Catalyst and its Application in Hydrolysis of hydrogen J. Luminescent journal 37 07-2

[10] Liu G, Niu P and Sun C 2010 Unique electronic structure induced high photoactivity of sulfur-doped graphitic C3N4 J. Journal of the American Chemical Society 132 11642-48

[11] Yeping L, Shilong W, Liying W, Junli W and Hui X 2014 Synthesis of carbon-doped g-C3N4 composites with enhanced visible-light photocatalytic activity J. Materials Letters 137 281-84

[12] Yan Z 2015 Study on the Modification and photocatalytic activity of Graphite-Like carbon Nitride g-C3N4 (Beijing: Beijing University of Technology)

[13] Wang H, Zhang X, Xie J and Zhang J 2015 Structural distortion in graphitic-C3N4 realizing an efficient photoreactivity J. Nanoscale 07 5152-56.

[14] Li J, Shen B, Hong Z and Lin B 2012 A facile approach to synthesize novel oxygen-doped g-C3N4 with superior visible-light photoreactivity J. Chemical Communications 48 12017-19.

[15] Yajun Z, Lingxia Z, Jianjun L and Xiangqian F 2015 Brand new P-doped g-C3N4: enhanced photocatalytic activity for H2 evolution and Rhodamine B degradation under visible light J. Journal of Materials Chemistry A 03 3862-3867

[16] Mo Z, Xiaojuan B, Di L and Jun W 2015 Enhanced catalytic activity of potassium-doped graphitic carbon nitride induced by lower valence position J. Applied Catalysis B Environmental 164 77-81

[17] Yali M, Ju S, Dan C and Gang X 2011 Photodegradation performance of methylene blue aqueous solution on Ag/g-C3N4 catalyst J. Rare Metals 30 276-79

[18] Xiaofeng S, Hong T, Liangxia C and Yan S 2014 Synthesis of Fe/g-C3N4 composites with improved visible light photocatalytic activity J. Materials Letters 116 265-67

[19] Chun C, Yu F, Meng H and Chunying W 2013 Photodegradation of bisphenol A by highly stable palladium-doped mesoporous graphite carbon nitride (Pd/mpg-C3N4) under simulated solar light irradiation J. Applied Catalysis B Environmental s142-143 553-60

[20] Zhang J, Ren F, Deng M and Wang, Y 2015 Enhanced visible-light photocatalytic activity of a g-C3N4/BiVO4 nanocomposite: a first-principles study J. Physical Chemistry Chemical Physics Peep 17 10218-26

[21] Oba F, Choi M, Togo A and Tanaka I 2011 Point defects in ZnO: an approach from first principles
[22] Fettkenhauer C, Clavel G, Kailasam K and Antonietti M 2015 Facile synthesis of new, highly efficient SnO2/carbon nitride composite photocatalysts for the hydrogen evolution reaction J. Green Chemistry 17 3350-61

[23] Kumar S, Baruah A, Tonda S and Kumar B 2014 Cost-effective and eco-friendly synthesis of novel and stable N-doped ZnO/g-C3N4 core-shell nanoplates with excellent visible-light responsive photocatalysis J. Nanoscale 06 4830-42

[24] Zhang J, Wang Y, Jin J and Zhang, J 2013 Efficient visible-light photocatalytic hydrogen evolution and enhanced photostability of core/shell CdS/g-C3N4 nanowires J. Acs Appl Mater Interfaces 05 10317-24

[25] Zhaojun P 2014 Experimental study on degradation of Rhodamine B catalyzed by Graphite Phase nitrogen Carbide by visible Light (Chengdu:Chengdu University of Technology)

[26] Liying H 2013 Study on preparation and degradation of Organic pollutants of visible Light-Responsive Graphite Phase carbon Nitride Composites (Jiangsu:Jiangsu University)

[27] Miszkiel J, Detka J, Cholewa J and Frankowska M 2013 Effect of graphitic carbon nitride microstructures on the activity and selectivity of photocatalytic CO2 reduction under visible light J. Catalysis Science & Technology 03 1253-1260

[28] Shaowen C, Xinfeng L, Yupeng Y and Zhenyi Z 2014 Solar-to-fuels conversion over In2O3/g-C3N4 hybrid photocatalysts J. Applied Catalysis B Environmental 147 940-46