Dean&Francis

ISSN 2959-6157

Graphitic Carbon Nitride Based Semiconductors and Their Applications in the Field of Photocatalysis

Yitong Li[1, *]

[1]Department of Mechanical Engineering, Chengdu University, Chengdu, China
*Corresponding author: 812010620@stu. hrbust. edu. cn

Abstract:

An increasing number of advanced semiconductor materials have been reported with the progress of theoretical and practical researches. The graphitic carbon nitride (g-C_3N_4) stands out as a highly promising semiconductor photocatalyst. It is known for its visible-light reaction and good chemical stability, indicating its potential for extensive use in photocatalysis. Recently, rapid progress has been made in researching g-C_3N_4-based semiconductor substances in photocatalysis. Till now, a large amount of work has focused on the applications of g-C_3N_4 in photocatalysis. This work focuses on those researches concerning with g-C_3N_4-based photocatalytic substances. Their structural characteristics, synthesis techniques, and efficiency enhancement are discussed in detail. Besides, their applications in different photocatalytic reactions are also highlighted. These reactions include hydrogen production by water decomposition, degradation of organic matter, carbon dioxide reduction, and photocatalytic bactericide. This article also points out the problems and challenges in the photocatalytic performance. Meanwhile, the stability of g-C_3N_4 is also highlighted. It also puts forward the promising research directions of g-C_3N_4 in the field of photocatalysis.

Keywords: Photocatalysis; g-C_3N_4; application; performance.

1. Introduction

In recent years, searching for sustainable and clean energy conversion technology has become the focus of scientific researches [1]. Photocatalysis is a green technology that converts light energy into chemical energy. It is energy efficient and environmentally friendly. There are various types of photocatalysts. Among them, g-C_3N_4 semiconductors shows good application prospects in photocatalysis due to their distinctive electronic structure and chemical properties [1].

It is widely recognized that g-C_3N_4, a non-metallic semiconductor, consists of carbon and nitrogen. Its energy band enables it to capture visible light. Additionally, it demonstrates the capacity to adsorb visible light and maintains remarkable thermochemical stability. Its unique electronic structure enables g-C_3N_4 to produce photoelectrons and holes under light conditions [1]. Because g-C_3N_4 can be prepared in various ways at relatively low cost [2], g-C_3N_4 is widely used in photocatalysis fields, such as hydrogen production by water decomposition [3], organic matter degradation [4, 5], and carbon dioxide reduction [6, 7].

Although g-C_3N_4 shows enormous applied value in the field of photocatalysis, its inherent low surface area ratio and high photogenerated carrier complexation rate limit the further improvement of its photocatalytic efficiency. Consequently, scientists have enhanced the catalytic efficiency of g-C_3N_4 through diverse methods, including the doping of heteroatoms and the creation of heterojunctions [2]. This work outlines the use of g-C_3N_4 in photocatalysis and focuses on its structures. Furthermore, this study also discusses the advancements in researching the photocatalytic characteristics of similar materials. Moreover, the issues and difficulties present in this studies are examined. Aiming to offer conceptual direction for the future creation and use of photocatalytic materials, this work would contribute to promote the practical application of photocatalytic technology.

2. Structure and Synthesis

The chemical composition of g-C_3N_4 is mainly composed of carbon and nitrogen elements, and its chemical formula is C_3N_4. Fig. 1 depicts the schematic configuration of g-C_3N_4. It is shown that two chemical configurations of g-C_3N_4 are illustrated in Fig. 1 which are g_1-C_3N_4 and g_2-C_3N_4. The g_1-C_3N_4 has the triazine ring (C_3N_3) as its structural segment with R3m space group. The g_2-C_3N_4 is characterized by the heptazine ring (C_6N_7) with P6m2 space group [1]. This structure gives g-C_3N_4 with good electron transport ability and stable chemical properties.

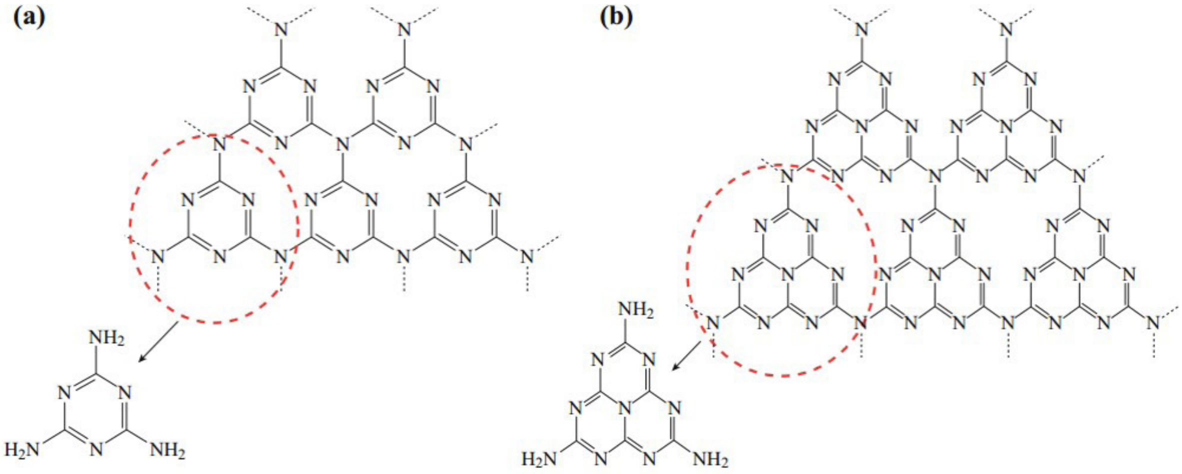

Fig. 1 Schematic structure of g-C_3N_4 [1].

The non-metallic photocatalytic compound g-C_3N_4 has a wider range of absorption rates than traditional TiO_2 photocatalysts. This substance is capable of photocatalyzing in regular visible light and exhibits intense absorption in the ultraviolet spectrum. Its extensive application in photocatalytic processes is attributed to its appropriate band gap and robust chemical stability. Additionally, g-C_3N_4 exhibits an indirect band gap from 2.7 eV to 2.9 eV. The C and N atoms undergo sp^2 hybridization, creating a π-π highly dispersed conjugated system [8]. This results in the semiconductor characteristics of this material.

At present, synthesis techniques of g-C_3N_4 are categorized into two types which are physical and chemical methods. Primarily, the physical techniques encompass ion implantation and the process of mechanical ball milling. These methods are generally used to produce g-C_3N_4 thin films and large amounts of powders [9]. Chemical methods are more commonly used in the preparation of g-C_3N_4 process. These methods include solvothermal method, microwave-assisted synthesis method, and thermal polycondensation synthesis method [1, 2]. For example, thermal polycondensation synthesis method [1] is to form g-C_3N_4 through deamination reaction by mixing precursors in non-metallic element dopants. Afterwards, thermal polymerization occurred directly in muffle or tube furnace at a specific temperature [10]. It is simple operation, low cost, and suitable for mass production. However, the purity of the product is low and the structural morphology is difficult to control. Another example is the microwave-assisted synthesis method [2]. The mixed raw materials are put into the microwave-assisted apparatus. The raw materials will be rapidly warmed up and polymerization reaction will take place under the microwave radiation. Microwave-assisted synthesis offers benefits such as energy-saving, high yield, superior purity, and the ability to manipulate product structures [11].

3. Photocatalytic Performance

Due to some shortcomings of g-C_3N_4, such as low photogenerated carrier mobility, low carrier separation efficiency and limited visible light influence range, researchers have suggested numerous methods to mitigate these flaws. Meanwhile, diverse approaches are explored to increase the photocatalytic efficiency of g-C_3N_4.

By constructing heterostructures based on g-C_3N_4, the energy band structure of g-C_3N_4 can be adjusted to enhance the light absorption and charge separation. Concurrently, this method can inhibit the merging of electron-hole pairs and enhance the efficiency of carrier separation. By this means, Fu et al. constructed an ultrathin heterostructures based on g-C_3N_4 which can eliminate the useless electrons and holes [12]. It is reported that the photocatalytic efficiency is highly enhanced.

The g-C_3N_4 energy band structure is adjusted by using metal or nonmetal doping to extend the light absorption region. By this way, both the light absorption in the band gap and the influence range of visible light can be increased. In addition, the redox under visible light can be promoted, thus making the photocatalytic performance of g-C_3N_4 enhanced. Zhang et al prepared Rb-g-C_3N_4 by heating in a water bath and firing at high temperatures [13]. Initial calculations and experiments reveal that within the 500 to 1100 nm wavelength spectrum, Rb-g-C_3N_4 outperforms pure g-C_3N_4 and other alkali-metal-doped g-C_3N_4 in absorption. In addition, superior CO_2 photo-reduction effects could be obtained in Rb-g-C_3N_4. Moreover, the production of CO exceeds that of pure g-C_3N_4 by over threefold.

Structural engineering techniques, including the regulation of shape and size, play a crucial role in enhancing mass transfer capabilities. Chen and colleagues crafted the porous g-C_3N_4 using a nickel-aided single-step thermal process [14]. The creation of nanosheets (PCN) was achieved through a single-step thermal process aided by Ni. Ni foam and H_2 further formed PCN by expanding the interlayer spacing and promoting pore formation. More active sites are exposed to facilitate the photogenerated charge and substrate transport rates through the pore channels.

4. Applications in Photocatalysis

4.1 Photolysis of Water to Hydrogen

In recent years, with the increasingly serious environmental and energy problems, hydrogen energy has become the research hotspot. As a novel type of photocatalytic material, g-C_3N_4 is increasingly employed in the photolysis of water for the generation of hydrogen. It has been demonstrated that g-C_3N_4 with a substantial specific surface area and a permeable structure can facilitate the formation of more active sites, thereby enhancing the photolytic water reaction. Chen et al. synthesised S and K co-doped g-C_3N_4 by self-assembling [3]. The results demonstrated that the rate of hydrogen production in the S and K co-doped g-C_3N_4 sample was 98 times greater than that observed in the non-doped g-C_3N_4 sample. The evident quantum efficiency (AQE) achieved at 420 nm reached as high as 70%. The photocatalytic activity of the as-prepared sample is enhanced. In addition, g-C_3N_4 can also be combined with other semiconductor materials to form heterojunctions and improve the efficiency of photolysis of water.

4.2 CO_2 Reduction

Furthermore, research is being conducted with the objective of utilising light energy for the purpose of reducing carbon dioxide and producing organic materials. This process helps to reduce the amount of CO_2 in the atmosphere and mitigate global warming. It can also converts light energy into green and renewable hydrocarbon fuels [7]. The catalytic reduction of CO_2 by g-C_3N_4 is influenced by various factors. In order to enhance the efficacy of solar fuels, Fu et al. prepared hierarchical porous carbon nitride nanotubes (OCN-Tubes) in an O-doped graphite phase by successive oxidative thermal exfoliation and convolution condensation [4]. The one-dimensional (1D) nanotube structure has the effect of increasing the specific surface area, thereby exposing a greater number of active sites. Meanwhile, O-doping replaces the N atoms in the g-C_3N_4 heterocycle, which changes the band structure of g-C_3N_4. It has been demonstrated that OCN-tube exhibits great photocatalytic activity under visible light. The methanol production rate of it is up to 0.88 $\mu\text{mol}\cdot g^{-1}\cdot h^{-1}$, while the methanol production rate of pure g-C_3N_4 is only 0.17 $\mu\text{mol}\cdot g^{-1}\cdot h^{-1}$. Besides, the doping of different non-metallic elements into g-C_3N_4 can significantly improve the efficiency of photo-reduction of CO_2 [1, 4].

4.3 Degradation of Qrganic Pollutants

It is well acknowledged that g-C_3N_4 has a strong redox capacity. It is widely used to degrade dyes, pesticides and antibiotics. Under light conditions, g-C_3N_4 is able to oxidize organic pollutants into water and carbon dioxide. Li et al. syntheticsed porous g-C_3N_4 by heat condensation polycondensation method with urea and ammonium chloride. The substance is employed for the purpose of degrading the dye rhodamine B (RhB) . The degradation of RhB basically reached up to 100% when it is exposed to light for 15 min [1, 15]. Modified carbon nitride degrades 16 times more efficiently on RhB than bulk carbon nitride. Although the soft template method is simple, it is susceptible to the calcination temperature [5]. Moreover, the template needs to be removed after use, which is easy to cause secondary pollution to the environment. Therefore, it is necessary to improve the method in the future.

4.4 Photocatalytic Sterilisation

In addition to organic pollutants, contamination of pathogens is also a major concern. Bacteria and viruses usually have strong adaptability to harsh environments. They are not easily inactivated. The g-C_3N_4 has broad-spectrum antimicrobial activity, which is capable of producing significant killing effects on a wide range of bacteria and viruses. Under light conditions, the shape of the virus is distorted. Therefore, the shell coat breaks down and the surface proteins are oxidised, leading to rapid leakage of the internal RNA genes. This ultimately leads to the complete death of the virus and the inability to regenerate [1]. At present, it is lack of studies on this field. Further research can be carried out in the future to explore more possibilities.

5. Conclusion

In summary, g-C_3N_4 has good application prospects in photocatalysis. As a non-metallic semiconductor material, it shows great applied value for application in photolysis of water to hydrogen, CO_2 reduction, and degradation of organic pollutants. By studying the synthesis, surface modification and modification of g-C_3N_4, its photocatalytic activity was significantly improved. However, g-C_3N_4 still faces some challenges in photocatalytic applications, such as limited light absorption range and high photogenerated carrier complexation rate. Therefore, exploring its photocatalytic mechanism is of great significance for promoting the practical application of g-C_3N_4 in photocatalysis.

References

[1] Z.Q. Zhang, Y.D. Sun, X. Zhang, et al. Progress in the preparation and application of non-metal-doped g-C_3N_4 photocatalytic materials. Materials Engineering, 2023, 51(12): 47-58.

[2] H.X. Du, J. Juan, C.W. Qin, et al. Progress in the preparation method of g-C_3N_4 and its photocatalytic performance enhancement pathway. Journal of Process Engineering, 2022, 22(02): 162-175.

[3] L. Chen, D.Y. Zhu, J.T. Li, et al. Sulfur and potassium co-doped graphitic carbon nitride for highly enhanced photocatalytic hydrogen evolution. Applied Catalysis B: Environmental, 2020, 273: 119050-119059.

[4] S.M. Lam, J.C. Sin,A.R. Mohamed, et al. A review on photocatalytic application of g-C_3N_4 /semiconductor (CNS) nanocomposites towards the erasure of dyeing wastewater. Materials Science in Semiconductor Processing, 2016, 47: 62-84.

[5] Q. Yan, C. Zhao, L. Zhang, et al. Facile two-step synthesis of porous carbon nitride with enhanced photocatalytic activity using a soft template. ACS Sustainable Chemistry & Engineering, 2019, 7(4): 3866-3874.

[6] J. Fu, B. Zhu, C. Jiang, et al. Hierarchical porous O-doped g-C_3N_4 with enhanced photocatalytic CO_2 reduction activity. Small Business Economics, 2017, 13(15): 1603938-1603984.

[7] M. Arumugam, M. Tahir, P. Praserthdam. Effect of nonmetals (B, O, P and S) doped with porous g-C_3N_4 for improved electron transfer towards photocatalytic CO_2 reduction with water into CH_4. Chemosphere, 286, 2022: 131765-131774.

[8] W.J. Ong, L.L. Tan, Y.H. Ng, et al. Graphitic carbon nitride based photocatalysts for artificial photosynthesis and environmental remediation: are we a step closer to achieving sustainability, Chemical Reviews, 2016, 116(12): 7159-7329.

[9] W.K. Yang, L.X. Lu, P. Li, et al. Synthesis, modification and application of graphitic phase carbon nitride as photocatalytic material. Journal of Petrochemical Higher Education, 2024, 37(1): 43-51.

[10] A. Sudhaik, P. Raizada, S. Thakur, et al. Peroxymonosulphate-mediated metal-free pesticide photodegradation and bacterial disinfection using well-dispersed graphene oxide supported phosphorus-doped graphitic carbon nitride. Applied Nanoscience, 2020, 10(11): 4115-4137.

[11] A. Kumar, Y. Kuang, Z. Liang, et al. Microwave chemistry, recent advancements, and eco-friendly microwave-assisted synthesis of nanoarchitectures and their applications: a review. Materials Today Nano, 2020, 11: 100076-100123.

[12] J.W. Fu, Q.L. Xu, J.X. Low, et al. Ultrathin 2D/2D WO_3/g-C_3N_4 step-scheme H_2-production photocatalyst. Applied Catalysis B: Environmental, 2019, 243: 556-565.

[13] H. Zhang, Y.Q. Tang, Z.X. Liu, et al. Study on optical properties of alkali metal doped g-C_3N_4 and their photocatalytic activity for reduction of CO_2. Chemical Physics Letters, 2020, 751: 137467-137473.

[14] X.R. Chen, Y. Zhang, D.S. Yuan, et al. One step method of structure engineering porous graphitic carbon nitride for efficient visiblelight photocatalytic reduction of Cr(VI). Journal of Materials Science & Technology, 2021, 71: 211-220.

[15] W. Li, X.C. Wu, X. Ma. Preparation of graphite phase carbon nitride g-C_3N_4 and its photocatalytic properties. Yunnan Chemical Industry, 2022, 49(10): 42-46.