



## Review

## Doping of graphitic carbon nitride for photocatalysis: A review



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## ABSTRACT

As a fascinating conjugated polymer, graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) has been the hotspot in the materials science as a metal-free and visible-light-responsive photocatalyst. Pure  $g\text{-C}_3\text{N}_4$  suffers from the insufficient sunlight absorption, low surface area and the fast recombination of photo-induced electron-hole pairs, resulting in low photocatalytic activity. Element doping is known to be an efficient method to tune the unique electronic structure and band gap of  $g\text{-C}_3\text{N}_4$ , which considerably broaden the light responsive range and enhance the charge separation. This review summarizes the recent progress in the development of efficient and low cost doped  $g\text{-C}_3\text{N}_4$  systems in various realms such as photocatalytic hydrogen evolution, reduction of carbon dioxide, photocatalytic removal of contaminants in wastewater and gas phase. Typically, metal doping, nonmetal doping, co-doping and heterojunction based on doped  $g\text{-C}_3\text{N}_4$  have been explored to simultaneously tune the crystallographic, textural and electronic structures for improving photocatalytic activity by enhancing the light absorption, facilitating the charge separation and transportation and prolonging the charge carrier lifetime. Finally, the current challenges and the crucial issues of element doped  $g\text{-C}_3\text{N}_4$  photocatalysts that need to be addressed in future research are presented. This review presented herein can pave a novel avenue and add invaluable knowledge to the family of element doped  $g\text{-C}_3\text{N}_4$  for the develop of more effective visible-light-driven photocatalysts.

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## 1. Introduction

The increasing global crisis of energy shortage and environmental issues are becoming serious threats to the sustainable development of human society. With outstanding merits including environmentally friendly and inexhaustible supply, sunlight has been served as the most ideal power to resolve the energy shortage and pollution removal. Particularly, semiconductor-based photocatalysis has been considered as a renewable, economic, safe, and clean technology, which conduct catalytic reactions for a variety of applications, such as water splitting [1–5], reduction of CO<sub>2</sub> [6–10], removal of organic pollutants [11–19], bacteria disinfection [20–22], and selective synthesis of organic compounds [23–26]. Nevertheless, the low solar-energy utilization efficiency and the wide band gap still remain the “bottleneck” of the photocatalysts to satisfy the requirements of practical applications [27]. For example, TiO<sub>2</sub> has become the most popular and widely used photocatalyst since Fujishima and Honda found that water can be split into hydrogen by using TiO<sub>2</sub> as photoanode in 1972 [28]. However, due to the fact that TiO<sub>2</sub> has broad bandgaps (~3.2 eV), the use of TiO<sub>2</sub> is limited by its poor performances under visible light irradiation. In order to achieve the practical use of photocatalysts and overcome the drawbacks of wide bandgap TiO<sub>2</sub>, various modified TiO<sub>2</sub> and TiO<sub>2</sub>-alternative photocatalysts with narrow bandgap, have been developed to efficiently utilize the visible light in solar light [29–34]. Currently, it is still a challenge to develop novel photocatalysts that are stable, abundant, efficient and facile in fabrication.

Recently, two-dimensional (2D) materials, graphene, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), transition-metal dichalcogenides, and hexagonal boron nitride with excellent properties have been widely used in optical and electronic devices, chemical sensors, energy generation and storage, as well as environmental remediation [35–42]. Particularly, g-C<sub>3</sub>N<sub>4</sub> has attracted intensive attention for its promising applications in photochemistry and photocatalysis as a metal-free polymer semiconductor with tri-s-triazine units [39,43,44]. In detail, g-C<sub>3</sub>N<sub>4</sub> is a medium band gap semiconductor with good visible light response (up to 460 nm). This suitable band gap, together with low cost, facile in preparation, high chemical stability, and pollution-free feature, is especially suitable for applications in photocatalytic organic pollutant degradation, water splitting, CO<sub>2</sub> reduction and organic synthesis under visible light [27,36,45–47]. However, the pristine g-C<sub>3</sub>N<sub>4</sub> is usually restricted by unsatisfactory photocatalytic efficiency due to the insufficient solar light absorption, low surface area and the fast recombination of photogenerated electron-hole pairs [39,48]. Generally, each photocatalytic reaction would involve three processes: photon absorption, electron-hole charges generation and separation, and catalytic surface reactions [49]. Therefore, various modification strategies, such as elemental and molecular doping [50,51], preparation of mesoporous g-C<sub>3</sub>N<sub>4</sub> [52], exfoliation to two-dimensional (2D) nanosheets [53], combination with conductive materials [54,55], nanocomposite structure construction with other semiconductors [43] and dye sensitization [56] are adopted to enhance the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>.

It is well known that g-C<sub>3</sub>N<sub>4</sub> owns tunable band gap with controllable lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [57]. It can remarkably affect the photoelectronic performance of g-C<sub>3</sub>N<sub>4</sub> as a functional photocatalytic nanosheet. Meanwhile, The tunable band gap of g-C<sub>3</sub>N<sub>4</sub>

simplifies the modification process mainly by element doping or heterojunctions structure construction [57]. Significantly, doping, that is designed by deliberately introducing impurities, is known to be an efficient method to tune the band gap of g-C<sub>3</sub>N<sub>4</sub>, which considerably broaden the light absorption and accelerate the electron-hole pairs separation. Doping of g-C<sub>3</sub>N<sub>4</sub> with P, S, C, I, or B via either interstitial or substitutional doping has been applied to modify its texture and electronic structure for enhancing the photocatalytic activity [58–62]. Also, alkali metals and transitional metals (K, Na, Fe, Cu, and W) have been incorporated into the framework of g-C<sub>3</sub>N<sub>4</sub> to enhance the photocatalytic performance [63–66]. Orbital hybridization occurs between the dopant orbital and the molecular orbital of g-C<sub>3</sub>N<sub>4</sub>, leading to a tunable electronic structure and potentials of valence band (VB) and conduction band (CB) [63,67].

Recently, the field of research and development of element doped g-C<sub>3</sub>N<sub>4</sub> photocatalysts is currently undergoing an exciting development with increasing achievements. In spite of several excellent reviews focusing on the synthesis and modification of g-C<sub>3</sub>N<sub>4</sub>-based photocatalysts and their applications in solving the energy and environmental issues [27,48,68–70]. However, only a handful of reviews have focused on the versatile properties and rational design of g-C<sub>3</sub>N<sub>4</sub>-based photocatalysts by doping. Element doping is considered as an efficient strategy to distinctly tune the optical, electronic, luminescent and other physical properties of g-C<sub>3</sub>N<sub>4</sub>. In the field of photocatalysis, band gap engineering of g-C<sub>3</sub>N<sub>4</sub> via the incorporation of cations, anions, or the codoping of both plays an excellent role to modulate the light absorption and redox band potentials for targeted photocatalytic applications. Thus, we believe that a comprehensive review on this subject is necessary to accelerate further developments. In this review, we intend to summarize the recent progress in the development of efficient and low cost doped g-C<sub>3</sub>N<sub>4</sub> systems in various realms such as photocatalytic hydrogen evolution, reduction of carbon dioxide, photocatalytic removal of contaminants in wastewater and gas phase. Finally, the current challenges and the crucial issues of element doped g-C<sub>3</sub>N<sub>4</sub> photocatalysts that need to be addressed in future research are presented.

## 2. Metal doping

Generally, the introduction of metallic impurities inflicts additional binding functions, which endows the doped system with unique photocatalytic properties by lowering the band gap and enhancing the absorption of visible light [63,64,71,72]. Table 1 summarizes metal-doped g-C<sub>3</sub>N<sub>4</sub> photocatalysts and their physicochemical properties, as well as photocatalytic performances. In order to import metal ions into the framework of carbon nitrides, the corresponding soluble salt is always uniformly mixed with the precursor of g-C<sub>3</sub>N<sub>4</sub>. In this way, metallic impurities will be simultaneously doped into the g-C<sub>3</sub>N<sub>4</sub> framework during the thermal condensation process of precursor.

### 2.1. Alkali metal

Alkali-metal ions such as K<sup>+</sup> and Na<sup>+</sup> were coordinated into the nitrogen pots of g-C<sub>3</sub>N<sub>4</sub> framework, which could remarkably ameliorate the transfer, transport and separation efficiency of charge carriers to induce a spatial charge-carrier distribution for enhanced photocatalytic redox reactions [63,73]. Hu et al. first prepared band gap-tunable potassium doped g-C<sub>3</sub>N<sub>4</sub> using dicyandiamide and

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