

Regular Article

Enhanced visible-light photocatalytic nitrogen fixation over semicrystalline graphitic carbon nitride: Oxygen and sulfur co-doping for crystal and electronic structure modulation



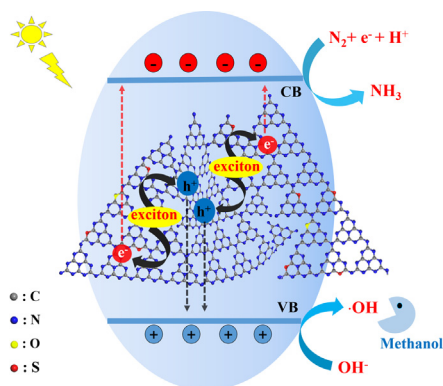
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GRAPHICAL ABSTRACT

O-S co-doped semicrystalline g-C₃N₄ was synthesised by a simple hydrothermal method. The obtained photocatalyst had high activity and stability in visible-light photocatalytic nitrogen fixation.



ARTICLE INFO

Article history:

Received 14 July 2017

Revised 30 August 2017

Accepted 7 September 2017

Available online 8 September 2017

Keywords:

Graphitic carbon nitride

Semicrystalline

Oxygen and sulfur co-doping

Electron structure

Visible-light photocatalytic nitrogen fixation

ABSTRACT

Oxygen and sulfur co-doped semicrystalline graphitic carbon nitride (HGCNOS) was synthesized by a one-pot hydrothermal method and applied in visible-light photocatalytic nitrogen fixation. Remarkably, HGCNOS exhibited a higher photocatalytic activity than pristine graphitic carbon nitride (GCN). Oxygen doping caused semicrystalline structure, making exciton dissociated at the order-disorder interfaces of HGCNOS and releasing more electrons and holes. Furthermore, the conduction band position of HGCNOS was elevated by sulfur doping, promoting the reduction ability of HGCNOS. Thus, the special electronic and physicochemical structure of HGCNOS contributed to the enhanced photocatalytic activity, facilitating its application on nitrogen photofixation.

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1. Introduction

Nitrogen fixation is one of the most important chemical processes in nature. Nitrogen element is required for the synthesis of biomolecules like proteins and nuclei acids, while most organisms are unable to metabolize natural nitrogen directly. The Haber-Bosch process is an artificial nitrogen fixation technology and ammonia is produced from the reaction of hydrogen and nitrogen. However, high pressure and temperature is required in the Haber-Bosch method, which limits its development in practical application. Therefore, it is considerable significant to investigate a low energy consumption and eco-friendly process to develop nitrogen fixation.

Photocatalysis, as an environmentally benign technology, has a great potential in nitrogen fixation [1,2]. To date, a variety of photocatalysts has been explored to realize photocatalytic nitrogen fixation. Schrauzer et al. [3] reported that the nitrogen could be reduced to ammonia by electrons generated from the light excitation of Fe doped TiO₂ powders. The reaction could be described as $6\text{H}_2\text{O} + 2\text{N}_2 \rightarrow 4\text{NH}_3 + 3\text{O}_2$. Janet et al. [4] synthesized Pt loaded hierarchical ZnO for nitrogen photofixation. The Pt metal played an important role in the activation of N≡N bonds, improving the efficiency of nitrogen fixation. However, these semiconductor materials mentioned can only be excited by ultraviolet light (5% of the solar light). Therefore, it is highly desired to explore efficient visible-light photocatalysts for nitrogen fixation recently. In order to enhance the nitrogen fixation efficiency under visible-light irradiation, Sun et al. [5] prepared ultrathin MoS₂ to accelerate nitrogen reduction reaction by introducing light induced trions. Li et al. [6,7] reported that oxygen vacancies of BiOCl and BiOBr nanosheets could absorb and active N₂, and transfer electrons as well, reducing the electron-hole recombination rate and improving the photocatalytic activity for nitrogen fixation. Meanwhile, Dong et al. and Wu et al. [8,9] reported that more nitrogen molecules could be absorbed on nitrogen vacancies and be reduced to NH₃ under visible-light irradiation. Until now, most of the photocatalysts used in nitrogen fixation were expensive and low abundant. Non-noble metals and even metal-free photocatalysts were expected to be used for the application of visible-light photocatalytic nitrogen fixation.

Graphitic carbon nitride (g-C₃N₄) has been deemed a promising heterogeneous metal-free semiconductor photocatalyst in recent years. It has attracted considerable attention due to its high physicochemical stability, appealing electronic structure, and appropriate band positions [10–13]. However, g-C₃N₄ is also subject to fast electron-hole recombination and low photocatalytic activity. Generally, the activity is greatly influenced by the structure, including of the crystal structure, electronic structure, and chemical structure [14]. Recently, many efforts for developing g-C₃N₄ have been made, such as crystal structure modulation [15], chemical structure adjustment [16], and electronic structure optimization [17]. Jürgens et al. [18] designed the crystal of g-C₃N₄ during condensation of melamine rings by using an ionothermal approach. Wirnhier et al. [19] prepared a high crystalline poly(triazine imide) (PTI)/Li⁺Cl⁻ using dicyandiamide in molten salts. More recently, Wang et al. [20] prepared semicrystalline g-C₃N₄ by a hydrothermal method using bulk g-C₃N₄ and ammonium chloride. It was emphasized that the exciton (bounded electron-hole pairs, which are formed by Coulomb interactions) dissociation could occur at the order-disorder interfaces in the semicrystalline g-C₃N₄. And the dissociated exciton in g-C₃N₄ could release electrons and holes, which could transfer to the ordered and disordered chains, respectively, developing the photocatalytic activity. In addition, Paquin et al. [21,22] also determined that excitons between crystalline (ordered) and amorphous (disordered) phases tended to dissociate in semicrystalline polymeric semiconductors.

The electronic structure of g-C₃N₄ could be optimized by doping with metal-free atoms to improve the photocatalytic performance [23–26]. For example, oxygen doped g-C₃N₄ could modulate electronic and band structure, and expand light absorbance range, enhancing the visible-light photocatalytic activity [27]. In our previous report, the photocatalytic activity of oxygen doped porous g-C₃N₄ was remarkably improved as compared to that of bulk g-C₃N₄ [28]. Liu et al. and Wang et al. [23,29] reported that sulfur doped g-C₃N₄ elevated the conduction band minimum and enhanced the conductivity of g-C₃N₄, thus improving the photocatalytic performance of g-C₃N₄. Besides of single-element doping, many co-doped g-C₃N₄, such as P–O co-doped g-C₃N₄ [30], O–S co-doped g-C₃N₄ [31], and P–S co-doped g-C₃N₄ [32] also presented excellent photocatalytic performance attributing to tailoring its electronic and optical properties. Compared to single-element doped g-C₃N₄, co-doped g-C₃N₄ photocatalysts combine the advantages of these dopants. Nevertheless, it is still a challenge to modify the crystal and electronic structure of g-C₃N₄ with bi-elements to make g-C₃N₄ an excellent photocatalyst for visible-light photocatalytic nitrogen fixation.

Herein, we developed a facile one-step hydrothermal treatment route to prepare O–S co-doped semicrystalline g-C₃N₄ (HGCNOS) for visible-light photocatalytic nitrogen fixation by treating g-C₃N₄ with L-cysteine. The chemical and electronic structure of HGCNOS significantly changed as compared to g-C₃N₄. Furthermore, the photocatalytic activity of HGCNOS in visible-light photocatalytic nitrogen fixation was evaluated. The results indicated that the exciton dissociation at the order-disorder interfaces and metal-free atoms doping synergistically led to the improved photocatalytic nitrogen fixation activity of HGCNOS.

2. Experimental section

2.1. Synthesis of the photocatalysts

2.1.1. The synthesis of GCN

GCN photocatalyst was synthesized with melamine as the precursor in a furnace, heating to 550 °C at a ramp rate of 2 °C/min and keeping for 4 h. The as-prepared yellow product was washed with ultrapure water and ethanol by several times and dried at 60 °C overnight to obtain GCN.

2.1.2. The synthesis of HGCNOS

HGCNOS complex was prepared by treating GCN with an L-cysteine assisted hydrothermal method. In a typical synthesis, L-cysteine (0.5 g) and 1 g GCN were dispersed in 100 mL water. Subsequently, the mixture was transferred into a 200 mL Teflon-lined autoclave, heated to 180 °C and maintained for 24 h. After cooling to room temperature, the product was filtered and washed with ultrapure water and ethanol for several times and dried at 60 °C overnight. The obtained powder was denoted as HGCNOS.

2.1.3. The synthesis of oxidized GCN (HGCNO)

HGCNO complex was prepared by treating GCN with a hydrothermal method. In a typical synthesis process, GCN (1.0 g) was dispersed in 100 mL water. Then, the mixture was transferred into a 200 mL Teflon-lined autoclave, heated at 180 °C for 24 h. After cooling to room temperature, the product was filtered and washed with ultrapure water and ethanol for several times and dried at 60 °C overnight. The obtained powder was denoted as HGCNO.

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