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Sulfur-doped graphitic carbon nitride decorated with zinc phthalocyanines towards highly stable and efficient photocatalysis

Qian Liang[a,*], Miao Zhang[a], Changhai Liu[b], Song Xu[a], Zhongyu Li[a,*]

[a] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, PR China

[b] Jiangsu Collaborative Innovation Center of Photovolatic Science and Engineering, School of Materials Science & Engineering, Changzhou University, Changzhou 213164, PR China

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ABSTRACT

A series of sulfur-doped graphitic carbon nitride (g-CNS) materials were prepared by thermal condensation of a high-quality thiourea and melamine under air atmosphere. When zinc phthalocyanine (ZnTNPc) was combined with g-CNS, the photocatalytic performance of ZnTNPc/g-CNS was 4.4 times higher than that of pure ZnTNPc under visible irradiation. More importantly, the ZnTNPc/g-CNS composites exhibited higher photocatalytic activity for the degradation of methylene blue than ZnTNPc/g-C_3N_4 under the same conditions. Some typical scavengers were added to identify the active species in the photocatalytic oxidation process. Mott-Schottky curve reveals that the introduction of sulfur atoms in the graphitic carbon nitride not only narrows the band gap but also results in a downshift of the conduction band. The mechanism of the enhanced photocatalytic activity of ZnTNPc/g-CNS is based on the synergetic effect between ZnTNPc and g-CNS, which causes a rapid photo induced charge separation and suppresses the possibility of recombination of electron-hole pairs. Our effects will provide a novel system to increase the number of active species participated in the photocatalytic process, and thus enhance the photocatalytic activity of carbon-based catalysts.

1. Introduction

With growing concerns regarding a clean environment and human health, technologies with high efficiency and low cost to reduce the pollutant contents of wastewater are urgently needed [1]. Various homogeneous and heterogeneous photocatalysts systems have been studied and employed in the past few decades [2–5]. However, low solar energy conversion efficiency and difficulties in separating for recycling limit the practical applications of these photocatalysts in environment purification. Thus, it is of great significance to search for non-toxic, low cost, stable and efficient visible light photocatalysts [6–9]. As typical organic semiconductors, Zinc phthalocyanine (ZnPc) and its derivatives possess wide visible light response. They can be synthesized with different substituent groups and coupled with other compounds by coordination or loading. Moreover, ZnPc is able to activate triplet oxygen into singlet oxygen ($^1O_2$), which is used as a non-radical oxidant for oxidizing organic pollutants [10]. And yet, the traditional phthalocyanine suffers from the aggregation ascribed to its intrinsic large π-conjugation [11]. To enhance the intrinsic properties of ZnPc for such applications, much work has focused on maximizing their active surface areas, and controlling their sizes by means of porous and stable semiconductors [12–15].

Graphitic carbon nitride (g-C_3N_4) polymers composed of covalent bonds have attracted considerable attentions due to their outstanding mechanical, electrical, thermal, and optical properties [16–18]. It is known that the band gap of g-C_3N_4 is about 2.7 eV, which can absorb visible light up to 450 nm [19–21]. However, it exhibits low photocatalytic activity because of the fast recombination of photogenerated charge carriers. In order to improve the photocatalytic activity, many strategies such as doping nonmetal element and coupling with other semiconductor are used to modify g-C_3N_4 [22–25]. In particular, sulfur-doped g-C_3N_4 could enhance the visible-light absorption of g-C_3N_4, improve its carrier mobility, or facilitate the separation of photogenerated electron-hole pairs [26]. For example, Xu et al. [27] prepared sulfur-doped g-C_3N_4 by means of pristine g-C_3N_4 and sulfur powder. Hong et al. synthesized mesoporous sulfur-doped g-C_3N_4 by using thiourea as the single sulfur source, and SiO_2 nanoparticles as the hard template

* Corresponding authors.
E-mail addresses: qianliang@cczu.edu.cn (Q. Liang), zhongyuli@mail.tsinghua.edu.cn (Z. Li).

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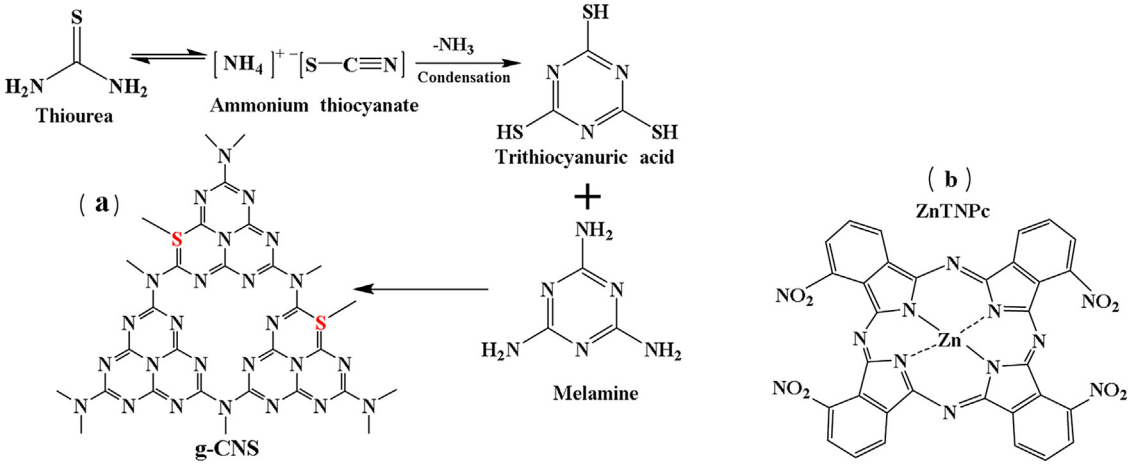

Fig. 1. Synthesis of sulfur-doped g-C_3N_4 from thiourea and melamine (a), molecular structure of ZnTNPc (b).

[28]. It has been shown that the different types of precursors and reaction pathways can affect the properties of g-C_3N_4, such as surface area, porosity and photocatalytic performances. Besides, ZnPc is similarly limited by the photocorrosion and fast recombination of the photogenerated charge carrier. For the purpose of designing the stable and efficient photocatalyst, combining the property of both sulfur-doped g-C_3N_4 and ZnPc to widen the spectral response seems extraordinarily vital.

Herein we report a facile and efficient approach to synthesize porous sulfur-doped g-C_3N_4 (CNS) by using both melamine and thiourea as precursors. The presence and position of sulfur in CNS sample were confirmed by XPS results, indicating that sulfur doped in the position of nitrogen to form C—S bond. The larger sulfur atom is expected to influence the conformation and photoelectric ability of g-C_3N_4 polymers. Furthermore, sulfur-doped g-C_3N_4 coupled with the zinctetranitrophthalocyanine (ZnTNPc) to prepare a photocatalyst (ZnTNPc/g-CNS) with the high surface area and extended spectral response in the whole visible wavelength range. The photocatalytic performances were evaluated by the degradation of MB under visible light irradiation. The stability of the ZnTNPc/g-CNS composite was analyzed, and the electronic band structures of g-CNS and g-C_3N_4 were investigated by electrochemical analysis. Moreover, some typical scavengers were added to identify the active species in the photocatalytic oxidation process, and the possible mechanism of photocatalytic activity enhancement by the synergic effect between CNS and ZnTNPc were also discussed systematically.

2. Experimental

2.1. Synthesis of g-C_3N_4

g-C_3N_4 sample was prepared as previous literature. In short, white melamine powder was placed in to alumina crucible and heated in air atmosphere at 550 °C for 4 h (the heating rate was 2.3 °C/min). Then the production was cooled to room temperature to obtain the g-C_3N_4 product.

2.2. Synthesis of g-CNS

The sulfur-doped g-C_3N_4 (g-CNS) was synthesized by a facile and efficient heating method. Melamine and thiourea was placed in an alumina crucible with a cover, and then heated in air atmosphere at 550 °C for 4 h (the heating rate was 2.3 °C/min). The resultant samples were denoted as g-CNS_x, where x refers to the nominal weight ratios of thiourea to melamine that were 30% (g-CNS_{30}), 60% (g-CNS_{60}) and 90% (g-CNS_{90}), respectively. After being naturally cooled to room temperature, sulfur-doped g-C_3N_4 of a yellow color was obtained.

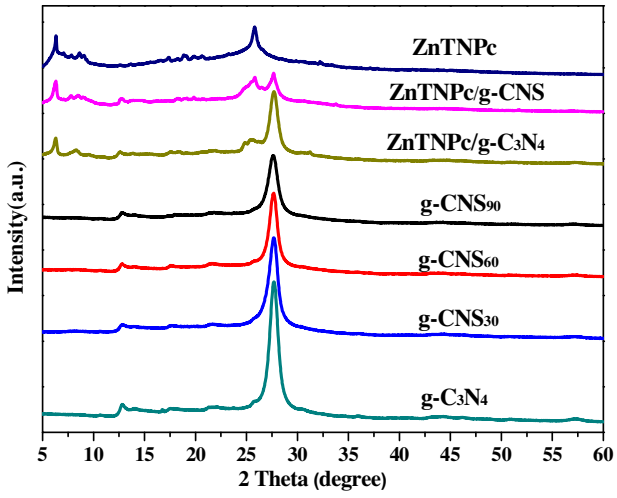

Fig. 2. XRD patterns of g-C_3N_4, g-CNS_{30}, g-CNS_{60}, g-CNS_{90}, pure ZnTNPc, ZnTNPc/g-C_3N_4 and ZnTNPc/g-CNS.

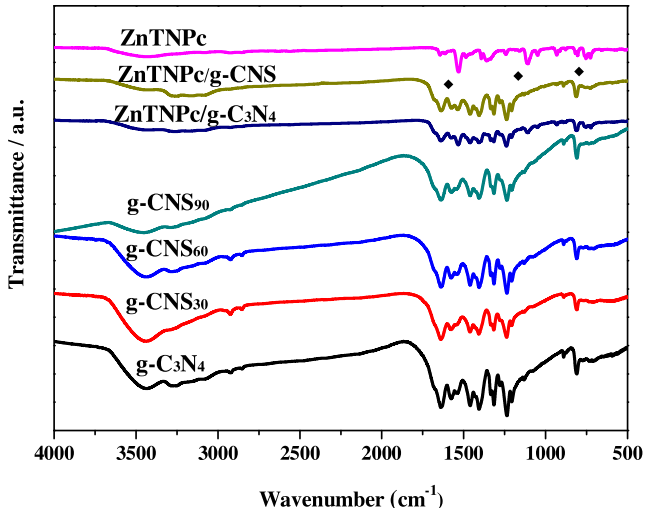

Fig. 3. FT-IR spectra of g-C_3N_4, g-CNS_{30}, g-CNS_{60}, g-CNS_{90}, pure ZnTNPc, ZnTNPc/g-C_3N_4 and ZnTNPc/g-CNS.