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High efficiency visible-light-driven Fe_2O_3-xS_x/S-doped g-C_3N_4 heterojunction photocatalysts: Direct Z-scheme mechanism

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ABSTRACT

Several nanoporous Fe_2O_3-xS_x/S-doped g-C_3N_4 (CNS) Z-scheme hybrid heterojuctions have been successfully synthesized by one-pot *in situ* growth of the Fe_2O_3-xS_x particles on the surface of CNS. The characterization results show that S-doping in the g-C_3N_4 backbone can greatly enhance the charge mobility and visible light harvesting capability. In addition, porous morphology of hybrid composite provides available open pores for guest molecules and also improves light absorbing property due to existence of multiple scattering effects. More importantly, the Fe_2O_3-xS_x nanoparticles formed intimate heterojunction with CNS and developed the efficient charge transfer by extending interfacial interactions occurred at the interfaces of both components. It has been found that the Fe_2O_3-xS_x/CNS composites have an enhanced photocatalytic activity under visible light irradiation compared with isolated Fe_2O_3 and CNS components toward the photocatalytic degradation of methylene blue (MB). The optimal loaded Fe_2O_3-xS_x value obtained is equal to 6.6 wt% that provided 82% MB photodegradation after 150 min with a reaction rate constant of 0.0092 min^{-1} which was faster than those of the pure Fe_2O_3 (0.0016 min^{-1}) and CNS (0.0044 min^{-1}) under the optimized operating variables acquired by the response surface methodology. The specific surface area and the pore volume of Fe_2O_3(6.6)/CNS hybrid are 33.5 m^2/g and 0.195 cm^3/g, which are nearly 3.8 and 7.5 times greater compared with those of the CNS, respectively. The TEM image of Fe_2O_3(6.6)/CNS nanocomposite exhibits a nanoporous morphology with abundant uniform pore sizes of around 25 nm. Using the Mott-Schottky plot, the conduction and valence bands of the CNS are measured (at pH = 7) equal to −1.07 and 1.48 V versus normal hydrogen electrode (NHE), respectively. Trapping tests prove that $^{\bullet}OH$— and $^{\bullet}O_2{}^{-}$ radicals are major active species in the photocatalytic reaction. It has been established that formation of the Z-scheme Fe_2O_3(6.6)/CNS heterojunction between CNS and Fe_2O_3 directly produces $^{\bullet}OH$ as well as $^{\bullet}O_2{}^{-}$ radicals which is consistent with the results obtained from trapping experiments.

1. Introduction

The rapid growing population and consequently increasing consumption of fossil fuels lead to unintended harmful emissions into the environment that is detrimental for the human health and ecological systems [1]. Semiconductor photocatalysis as an eco-friendly technology using the clean solar energy has attracted great interest worldwide for environmental protection and energy production [2–5]. TiO_2 is the well-known semiconductor which was broadly used for the photocatalytic degradation of organic contaminants in 1976 [6]. However, TiO_2 is only able to absorb 3%–5% of sunlight irradiated in the ultraviolet range, which deeply restricts its extensive applications [7,8]. Therefore, the design of stable, eco-friendly and visible-light-active photocatalysts can overcome the mentioned obstacle for realistic applications.

Among photocatalysts explored, the graphitic carbon nitride (g-C_3N_4) is known as a metal-free semiconductor that only contains carbon and nitrogen elements and can be extremely easily achieved through polycondensation/polymerization of cheap raw materials such as cyanamide, urea, melamine and dicyandiamide [9]. In addition, g-C_3N_4 is considered as an inexpensive photocatalyst with the relatively narrow band gap of 2.70 eV so that it absorbs the visible light around 450–460 nm [10]. These properties denote that the g-C_3N_4 has promising applications for the photocatalytic

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degradation of organic wastewater pollutants [11]. Nevertheless, the bulk g-C_3N_4 still suffers from several intrinsic obstacles including small surface area (<10 m^2/g), fast recombination of charge carriers and lack of absorption above 460 nm [12]. To overcome these bottlenecks, various attempts have been accomplished in order to rationally design and develop approaches for improving photocatalytic activities of g-C_3N_4 materials. Since g-C_3N_4 has a polymeric nature, it is possible to modify its surface chemistry without obviously changing the theoretical structure [13]. Various surface engineering strategies have been used such as doping of non-metal (B [14,15], S [16] and O [17]) and metal (Fe [18,19] and Cu [20]) elements, nanoarchitecture preparation through soft/hard templating methods, supramolecular preorganization [21] as well as designing g-C_3N_4/metal oxide heterojunction (g-C_3N_4/TiO_2 [22], g-C_3N_4/WO_3 [23] and g-C_3N_4/Fe_2O_3 [24]). Moreover, it has been reported that type of starting materials (such as urea, melamine, dicyandiamide, etc.) as well as the actual pyrolysis duration (i.e. additional thermal treatment) intensely affects the photoactivity of such materials [25].

One of the most favorable approaches to improve the light-absorbing property of bulk g-C_3N_4 and to engineer its electronic structure is homogeneous anion doping at the atomic level [26–32]. Indeed, according to density functional theory (DFT) calculation, dopants form midgaps between valance and conduction bands and facilitate separation of the electron-hole pairs generated under light irradiation. Liu et al. obtained *ex situ* S-doped g-C_3N_4 via treating the g-C_3N under H_2S gaseous atmosphere at 450 °C. They found that photocatalytic activity of $C_3N_{4\text{-}x}S_x$ for H_2 evolution under visible light irradiation was 8.0 times greater compared with that of bulk g-C_3N_4 [26]. However, it is believed that this method produces much poisonous gas and use of H_2S is not environmentally benign. Hong et al. synthesized *in situ* S-doped mesoporous g-C_3N_4 (mpgCNS) from thiourea as an inexpensive and easily accessible precursor using hard-template method [33]. The mpgCNS showed 30 times superior photocatalytic activity for the H_2 production relative to that of pure g-C_3N_4. Very recently, the S-doped g-C_3N_4 (CNS) photocatalyst was simply achieved through heating the thiourea and melamine mixture [33] and it was exhibited that the photocatalytic CO_2 reduction using the CNS was 1.38 times greater in comparison to that of pure g-C_3N_4 under UV–vis light irradiation. Even though the S-doping improved the photocatalytic activity of bulk g-C_3N_4 especially for water splitting [34] and CO_2 reduction [35], the photocatalytic degradation reaction of organic pollutants by visible light irradiation using S-doped g-C_3N_4 as the photocatalyst is scarce in the literature [36].

The coupling of g-C_3N_4 with other available semiconductors is an alternative satisfactory approach to engineer the physicochemical characteristics of g-C_3N_4 materials. Certainly, combining the g-C_3N_4 with another semiconductor which has well-matching conduction (CB) and valence band (VB) edge potentials with respect to g-C_3N_4, leads to creating heterojunction at the interface of two components. This approach is originated from the possible variations between two compounds forming band bending at their interfaces. Thus, the phenomenon induces an internal electric field at depletion layer and results in accelerating an efficient charge transfer and separation [13].

Among the semiconductors, Fe_2O_3 is a non-toxic, low cost and abundant material possessing a narrow band gap energy (about 2.2 eV) that can absorb most of the visible light [24,37]. However, rapid recombination of the photogenerated electron-hole pairs restricts its further application as an efficient photocatalyst. It is documented that iron oxide has a band gap with CB and VB edge potentials near 0.49 eV and 2.29 eV, respectively, that are smaller compared with those of the g-C_3N_4 photocatalyst [38]. In theory, the g-C_3N_4 well matches with Fe_2O_3 and forms type II heterojunction at their interface. Considering this subject, Christoforidis and coworkers synthesized Fe_2O_3/g-C_3N_4 composites via a facile *in situ* growth method using a solid state process which demonstrated the utmost photocatalytic performance for the pollutant decomposition compared with those of the isolated Fe_2O_3 and g-C_3N_4 [37]. Recently, composite materials of the g-C_3N_4 coupled with iron oxide have effectively been utilized for environmental remediation [39,40].

On the basis of the above concepts, it is expected that if two simultaneous approaches including the elemental non-metal doping and hybridization of another semiconductor are applied, some intrinsic bottlenecks of g-C_3N_4 such as the limited visible light absorption ability and high recombination of charge carriers could well be overcome. In this context, most recently, Kong et al. coupled S-doped g-C_3N_4 with $BiVO_4$ by impregnation precipitation process and the prepared composite indicated an O_2 evolution rate equal to 750 $\mu mol\,h^{-1}g^{-1}$ which was higher relative to that of the pure $BiVO_4$ [41].

In this work, nanoporous Fe_2O_3-xS_x/S-doped g-C_3N_4 (CNS) composites have been synthesized by means of two concurrent routes which are S-doping and creating hybrid structures. The nanocomposite photocatalysts having diverse amounts of Fe_2O_3-xS_x are readily achieved by an *in situ* growth process through thermal condensation of thiourea in presence of iron(III) nitrate. The X-ray diffraction (XRD), nitrogen adsorption/desorption, Fourier-Transfoem infrared (FT-IR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and diffuse reflectance spectroscopy (DRS) techniques have been used for the characterization of the nanophotocatalysts with dissimilar Fe_2O_3-xS_x loadings. The effects of Fe_2O_3 amount and reaction operating factors on the photocatalyst efficiency are also assessed. The synthesized Fe_2O_3-xS_x/CNS Z-scheme nanostructured heterojuctions display exceptional photocatalytic performances for the visible light photodegradation of methylene blue (MB). Further, radical trapping experiments have been accomplished in order to explore the reason for the high photocatalytic efficacy and the reaction mechanism.

2. Experimental

2.1. Synthesis of Fe_2O_3-xS_x/CNS photocatalysts

First, 2 g thiourea was dissolved in 10 mL deionized water and heated at 60 °C under stirring condition. Next, an appropriate amount of iron(III) nitrate nonahydrate (0.01, 0.05 or 0.08 g) was added to the thiourea solution, and the reaction flask contents were subjected to the ultrasonic irradiation for 30 min. The resulting solution was heated to 100 °C in an open system to evaporate water. The powder compound was dried at 80 °C and then it was annealed in a muffle furnace at 535 °C for 3 h under air atmosphere (heating rate was 3 °C min^{-1}). The final Fe_2O_3-xS_x/CNS composites with various Fe_2O_3-xS_x contents were designated as Fe_2O_3-$xS_x(y)$/CNS, where y was the weight percent (wt%) measured using the thermogravimetric analysis (TGA) analysis. For comparison, S-doped g-C_3N_4 (CNS) was obtained by the above-mentioned route in the absence of $Fe(NO_3)_3 \cdot 9H_2O$ to examine the influence of S-doping on the photocatalytic performance of composite. The Fe_2O_3 nanoparticles were synthesized with an analogous method without using g-C_3N_4. In addition, the bulk g-C_3N_4 powder was synthesized through dicyandiamide heating by the technique defined elsewhere [42].

2.2. Experimental design

The design of experiment is necessary to obtain adequate and reliable measurements for the responses of interest. The response