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The effects of bismuth (III) doping and ultrathin nanosheets construction on the photocatalytic performance of graphitic carbon nitride for antibiotic degradation

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GRAPHICAL ABSTRACT
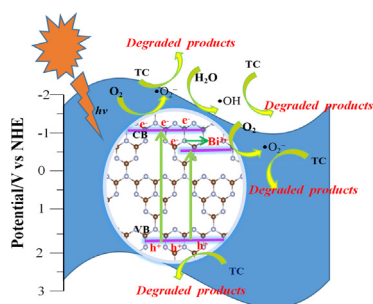
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ABSTRACT

To further enhance the photocatalytic performance of graphitic carbon nitride (g-C$_3$N$_4$), we rationally combined two strategies (foreign metal doping and ultrathin nanosheet construction) to synthesize bismuth (III) (Bi^{3+}) doped ultrathin g-C$_3$N$_4$ nanosheets (Bi-CNNS) via one-step thermal polymerization method using melamine as the raw material, bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O) as the dopant source, and nitric acid (HNO$_3$) and acetic acid (AC) as soft templates for the ultrathin nanosheets construction. The Bi-CNNS catalysts exhibited an excellent photocatalytic performance in tetracycline (TC) degradation. The TC removal efficiency reached to be 94.1% in 30 min under visible-light irradiation over 0.03Bi-CNNS, which is 6.03 times higher than that of pure g-C$_3$N$_4$ (CN). The higher specific surface area, narrower bandgap, the improved photoexcited electron-hole pair transfer and separation efficiency, and prolonged carrier lifetimes in the Bi^{3+}-doped ultrathin g-C$_3$N$_4$ nanosheets led to a significantly enhanced photocatalytic performance. The main radical species responsible for the degradation of tetracycline over 0.03Bi-CNNS were ·O$_2^-$ and ·OH. Moreover, the possible photodegradation intermediate products of TC were detected by gas chromatography–mass spectroscopy (GC–MS), and a possible pathway was proposed.

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1. Introduction

Tetracycline (TC) is a broad-spectrum antibiotic that has been widely used for the treatment of a broad range of human and animal infections in the past decades [1]. Because of its continuous overuse, TC causes antibiotic resistance, which has drawn widespread concern in society, and has often been detected in the environment [2]. TC removal from wastewater by conventional wastewater treatment methods, including adsorption and biodegradation, is difficult and inefficient because TC is a stable, toxic, and biorefractory compound [3–5]. Therefore, new and

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efficient techniques for the removal of TC from wastewater are urgently needed.

Recently, semiconductor photocatalysts have been widely concerned in TC removal from wastewater because of their environmental friendliness, excellent degradation efficiency, thorough degradation properties, lower secondary pollution generation, and shorter periods [6–9]. The traditional photocatalyst TiO_2 has been widely used due to its outstanding photocatalytic efficiency and chemical stability. However, TiO_2 photocatalysts can only utilize ultraviolet light, which only accounts for about 4% of the solar light spectrum, thus restricting their practical application [10]. Therefore, developing visible-light-excited photocatalysts is vital and needed for the photocatalytic treatment of TC.

Graphitic carbon nitride (g-C_3N_4) is a novel polymer semiconductor that has been widely exemplified as a promising visible-light-driven photocatalyst due to its narrow bandgap of ~2.7 eV, which can be excited by visible-light illumination. However, the pristine g-C_3N_4 prepared by the thermal polymerization of nitrogen-rich precursors exhibits unsatisfactory photocatalytic performance for practical applications because of its relatively large bandgap and poor specific surface area [11–18]. Therefore, it is urgently needed to solve these issues in g-C_3N_4 to develop g-C_3N_4-based semiconductor photocatalysts with high photocatalytic efficiency. Therefore, many strategies, such as foreign metal and non-metal ion doping [19–21], composite construction [21–23], and surface area enhancing through constructing mesoporous structure and/or nanostructures [24], have been adopted to enhance the photocatalytic efficiency of g-C_3N_4 catalysts.

Among those strategies, foreign metal doping is one of the most adopted and effective ways to promote the photocatalytic performance of g-C_3N_4 photocatalysts, as it can reduce the bandgap, improve the visible-light harvest ability, and promote the transfer and separation of electron-hole pairs [24]. So far, many metals, including K [25], Na [26], Co [27], Mo [28], Eu [29], Ce [30], Fe [31], W [32], Cu [33], Zr [34], and so forth, have been chosen to dope g-C_3N_4 to promote its visible-light-induced photocatalytic performance. However, to the best of our knowledge, rare study on Bi^{3+} doped g-C_3N_4 have been reported up to now.

In addition to doping with foreign metal elements, ultrathin nanosheet construction is another direct and effective way to promote the photocatalytic activity of g-C_3N_4. Ultrathin nanosheets exhibit excellent charge carrier transfer and separation efficiencies and provide numerous active sites, which originate from their higher specific surface area, compared to bulk g-C_3N_4 [24,35,36]. Ultrathin g-C_3N_4 nanosheets are usually obtained by acid post-treatment, the second thermal oxidation etching, chemical exfoliation, and so on [28–30], which are not eco-friendly or low-cost approaches. Therefore, there is an urgent need to explore an environmentally friendly and facile strategy to prepare ultrathin g-C_3N_4 nanosheets.

However, it is noteworthy that a single strategy, for instance, only doping or only nanostructure construction, cannot simultaneously solve the afore mentioned shortcomes in g-C_3N_4; therefore, a combination of those two strategies is necessary. Herein, to enhance the photocatalytic activity of g-C_3N_4, Bi^{3+} doped ultrathin g-C_3N_4 nanosheets (Bi-CNNS) were fabricated in current study via a one-step thermal polymerization method using melamine as raw materials, $Bi(NO_3)_3·5H_2O$ as a foreign dopant source, and HNO_3 and CH_3COOH (AC) as soft templates for the ultrathin nanosheets construction. As far as we know, Bi^{3+} doped ultrathin g-C_3N_4 nanosheet catalysts have rarely been reported before. The crystal structure, morphology, specific surface area, surface chemical states, light harvest ability, and photoluminescence of the as-prepared Bi^{3+} doped ultrathin g-C_3N_4 nanosheet photocatalysts were studied, and the photocatalytic activity towards TC degradation was measured. The Bi^{3+} doped ultrathin g-C_3N_4 nanosheets

exhibit superior photocatalytic activity towards TC compared to the non-doped g-C_3N_4 sample. Moreover, the main intermediates produced during TC degradation were detected by gas chromatography–mass spectroscopy(GC–MS), and the possible degradation pathway was also analyzed. This work might offer a promising new strategy to develop g-C_3N_4 photocatalysts with high-performance for TC degradation.

2. Experimental details

2.1. Materials

Melamine ($C_3H_6N_6$, >99.0%), $Bi(NO_3)_3·5H_2O$ (>99.0%), HNO_3 (99.0%), and acetic acid (AC, 99.0%) were purchased from Tianjin Kermel Chemical Reagent Co. Ltd, China, tetracycline (TC, >99.0%) was bought from Shanghai Aladdin Reagent Co., Ltd. 1,4-benzoquinone (BQ, >99.0%), ammonium oxalate (AO, >99.0%), iso-propanol (IPA, >99.0%) were bought from National Drug Group Chemical Reagent Shenyang Co., Ltd, China. All reagents were of analytical grade and used as received without further purification, and the deionized water was used in the experiments.

2.2. Photocatalyst preparation

The thermal polymerization method was employed to prepare the Bi^{3+} doped ultrathin g-C_3N_4 nanosheet photocatalyst. Typically, 4.0 g melamine, some amount of $Bi(NO_3)_3·5H_2O$ (0.015 g, 0.03 g, 0.045 g), and 4 mL AC (36%) and 5 mL HNO_3 (60%) were mixed together and put into a 300-mL crucible with a cover. The precursor was calcined at 520 °C for 2 h in a muffle furnace. Then, the crucible was removed immediately and naturally cooled to room temperature to obtain the target products. The obtained samples with different weights of $Bi(NO_3)_3·5H_2O$ (x = 0.015 g, 0.03 g, and 0.045 g, respectively) were labeled as xBi-CNNS, i.e., 0.015Bi-CNNS, 0.03Bi-CNNS, and 0.045Bi-CNNS, respectively.

For comparison, non-doped pristine g-C_3N_4 was prepared under the same conditions except for the use of $Bi(NO_3)_3·5H_2O$ and was labeled as CN.

To investigate the effect of AC and HNO_3 on the formation of ultrathin nanosheets, the bulk Bi^{3+}-doped g-C_3N_4 with 0.03 g of $Bi(NO_3)_3·5H_2O$ was also prepared by the same procedure, except for AC and HNO_3 addition. The corresponding sample was labeled 0.03Bi-BCN. Moreover, pure bulk g-C_3N_4 was also prepared without $Bi(NO_3)_3·5H_2O$ addition and was labeled BCN.

2.3. Characterization

The surface chemical states and elemental compositions of the catalysts were detected by X-ray photoelectron spectroscopy (XPS; Thermo VG Scientific). The crystal structure and phase composition of the as-prepared catalysts were investigated by powder X-ray diffraction (XRD; D/MAX-2500) with Cu Kα radiation and a Fourier transform infrared spectroscopy (FT-IR; Bruker). The morphologies and structures of the as-prepared catalysts were studied by transmission electron microscopy (TEM; JEM-2100F), scanning electron microscopy (SEM; Hitachi (S-3400)) and atomic force micro-scopy (AFM, Bruker). A nitrogen adsorption apparatus (ASAP 2020, USA) was employed to determine the specific surface area of the catalysts through the Brunauer-Emmett-Teller (BET) method. The optical properties of the catalysts were measured on a U-3010 UV–vis spectrometer with $BaSO_4$ as reference and a Hitachi-4600 fluorescence spectrometer. The electron spin resonance (ESR) of the captured free radicals was investigated on a Bruker ER200-SRC spectrometer with 5,5-dimethyl-l-pyrroline N-oxide (DMPO) as quencher under visible-light illumination