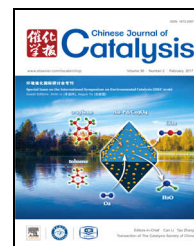


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Enhanced visible-light photo-oxidation of nitric oxide using bismuth-coupled graphitic carbon nitride composite heterostructures

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ABSTRACT

Pure bismuth (Bi) metal-modified graphitic carbon nitride (g-C₃N₄) composites (Bi-CN) with a pomegranate-like structure were prepared by an *in situ* method. The Bi-CN composites were used as photocatalysts for the oxidation of nitric oxide (NO) under visible-light irradiation. The inclusion of pure Bi metal in the g-C₃N₄ layers markedly improved the light absorption of the Bi-CN composites from the ultraviolet to the near-infrared region because of the typical surface plasmon resonance of Bi metal. The separation and transfer of photogenerated charge carriers were greatly accelerated by the presence of built-in Mott–Schottky effects at the interface between Bi metal and g-C₃N₄. As a result, the Bi-CN composite photocatalysts exhibited considerably enhanced efficiency in the photocatalytic removal of NO compared with that of Bi metal or g-C₃N₄ alone. The pomegranate-like structure of the Bi-CN composites and an explanation for their improved photocatalytic activity were proposed. This work not only provides a design for highly efficient g-C₃N₄-based photocatalysts through modification with Bi metal, but also offers new insights into the mechanistic understanding of g-C₃N₄-based photocatalysis.

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1. Introduction

The potential for noble metal-based materials to harvest and convert solar energy has garnered considerable attention in recent years [1–3]. In particular, the ability of noble metals to strongly absorb visible light because of their localized surface plasmon resonance (SPR), which considerably increases their

utilization efficiency of visible light, is important for their application [4,5]. In view of expense of precious metals, some affordable and readily available metals possessing similar electronic and light-absorption characteristics to those of noble metals have been investigated as substitutes [6–10]. It is well documented that the semimetal bismuth (Bi) behaves as a photocatalyst with promising photocatalytic performance [10].

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Pure Bi metal can exhibit admirable photocatalytic reactivity under ultraviolet (UV) irradiation ($\lambda \leq 280$ nm), but its response to visible light is poor [11]. Thus, it is important to develop feasible and environmentally benign strategies to afford Bi with visible-light activity.

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) can photocatalytically break down various pollutants into harmless chemicals and photocatalyze water conversion to hydrogen and hydrogen peroxide under visible-light irradiation [12–15]. However, the photocatalytic efficiency of bulk $g\text{-C}_3\text{N}_4$ is quite low because of its marginal absorption of visible light and poor separation of photogenerated carriers; therefore, effective modification methods need to be developed to improve its visible-light performance. For this reason, a number of $g\text{-C}_3\text{N}_4$ -based heterostructures with synergetic coupling effects between $g\text{-C}_3\text{N}_4$ and other functional materials have been developed to greatly enhance its absorption of visible light and facilitate charge transfer [16–18]. Recently, Dong et al. [19] synthesized Bi nanosphere-modified $g\text{-C}_3\text{N}_4$ nanosheets ($\text{Bi-g-C}_3\text{N}_4$) with excellent photocatalytic performance. The as-obtained $\text{Bi-g-C}_3\text{N}_4$ composites combined with some bismuth oxide (Bi_2O_3) layers offered two major advantages over pure $g\text{-C}_3\text{N}_4$ in photocatalytic reactions. On one hand, by loading Bi metal on the surface of $g\text{-C}_3\text{N}_4$, Bi-coupled $g\text{-C}_3\text{N}_4$ nanocomposites with a strong visible-light response were obtained because of the SPR effects of Bi. On the other hand, the supporting Bi nanospheres accelerated the separation of photogenerated charge carriers because of the formation of a Mott-Schottky barrier at the $\text{Bi/g-C}_3\text{N}_4$ interface. However, Bi_2O_3 formed on the surface of $\text{Bi-g-C}_3\text{N}_4$ composites can have a shielding effect that deteriorates the above-mentioned contributions from Bi. Dong and colleagues [19] used bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) as the precursor for Bi metal, but the oxidizing ability endowed by NO_3^- led to the generation of Bi_2O_3 in the resultant composites. Along this line of thinking, it is necessary to prepare pure Bi metal-coupled $g\text{-C}_3\text{N}_4$ composites without Bi_2O_3 layers by using a substitute for $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

Nitric oxide (NO) and nitrogen dioxide (NO_2), jointly referred to as NO_x , are typical indoor and outdoor air pollutants that are causing increasing environmental concern. NO_x is one of the major contributors to acid rain and urban smog, and could result in serious respiratory diseases, hospitalization for heart or lung diseases, and even premature death [19].

In the present study, pure Bi metal-modified $g\text{-C}_3\text{N}_4$ (Bi-CN) composites are fabricated by an in situ grafting treatment. These composites show high reactivity in photo-oxidation of NO under visible-light illumination. Sodium bismuthate ($\text{NaBiO}_3 \cdot 2\text{H}_2\text{O}$) is successfully used as a precursor of Bi metal to obtain pure Bi metal in the Bi-CN composites. The composites are investigated by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The photo-oxidation of NO by the Bi-CN composites is evaluated.

2. Experimental

2.1. Preparation of Bi-CN composites

All chemicals were of analytical grade and used without further purification. We synthesized $g\text{-C}_3\text{N}_4$ by heating dicyanamide (20 g) at 550 °C for 2 h. To synthesize the Bi-CN composite photocatalysts, $\text{NaBiO}_3 \cdot 2\text{H}_2\text{O}$ (0.339 g) was completely dissolved in ethylene glycol (EG, 30 mL) under continuous magnetic stirring and then polyvinylpyrrolidone (PVP, MW 130,000, 0.2 g) was added. The molar ratio of Bi to the repeating unit of PVP was controlled at 1:1.6. A certain amount of $g\text{-C}_3\text{N}_4$ was then added to the solution under vigorous stirring. After stirring for 1 h, the mixture was transferred into a 100-mL Teflon-sealed autoclave, sealed and heated at 200 °C for 24 h in a furnace, before cooling to room temperature. The product was centrifuged, and then washed with acetone followed by ethanol several times to remove residual EG and PVP. Bi-CN photocatalysts with different weight ratios of metallic Bi to CN (namely, 5% Bi-CN, 10% Bi-CN, 15% Bi-CN, 25% Bi-CN, and 50% Bi-CN) were synthesized. Metallic Bi and solvothermally prepared $g\text{-C}_3\text{N}_4$ (CN-EG) were also prepared as reference samples, using the same procedure as that for the Bi-CN composites except that only either $g\text{-C}_3\text{N}_4$ or Bi was added.

2.2. Characterization

The phase structures of the samples were investigated by XRD (D/max RA, Japan). The morphological characteristics and microstructures of the samples were characterized with a scanning electron microscope (SEM; JEOL JSM-6490, Japan). Nitrogen adsorption-desorption isotherms were obtained using a nitrogen adsorption apparatus (ASAP 2020, USA), in which all of the samples were degassed at 150 °C prior to the measurements to investigate their surface areas and pore size distributions. Samples embedded in KBr pellets were subjected to FT-IR spectroscopy in a Nicolet Nexus spectrometer to detect the functional groups on their surfaces. The surface chemical composition and total density of state distribution in the valence band (VB) of each sample were probed using an X-ray photoelectron spectrometer (Thermo ESCALAB 250, USA) with Al K_α X-rays ($h\nu = 1486.6$ eV) operated at 150 W. The shift of the binding energy attributed to relative surface charging was corrected using the C 1s level at 284.8 eV as an internal standard. The optical properties of the samples were measured by an ultraviolet-visible diffuse reflectance spectrophotometer (UV-Vis DRS; UV-2450, Shimadzu, Japan) equipped with an integrating sphere assembly; BaSO_4 was used as the reflectance sample. Photoluminescence (PL) spectra of the samples were obtained with a fluorescence spectrophotometer (FS-2500, Japan) using a Xe lamp with an optical filter as the excitation source to investigate the recombination and separation of photogenerated electrons and holes.

2.3. Visible-light photocatalytic activity.

The photocatalytic activity of the samples was evaluated through the oxidation of NO at the 10^{-6} level in a continuous-flow reactor at ambient temperature. The volume of the rectangular reactor composed of stainless steel and covered with quartz glass was 4.5 L ($30 \times 15 \times 10$ cm). An LED lamp

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