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Research paper

Designing all-solid-state Z-Scheme 2D g-C_3N_4/Bi_2WO_6 for improved photocatalysis and photocatalytic mechanism insight

Mao Mao [a], Shuowei Zhao [b], Zhigang Chen [a], Xiaojie She [a], Jianjian Yi [a], Kaixiang Xia [a], Hui Xu [a], Minqiang He [a,*], Huaming Li [a,*]

[a] *School of Chemistry and Chemical Engineering, Institute for Energy Research, Jiangsu University, Zhenjiang 212013, China*
[b] *Institute of Environmental Science, Zhenjiang, Jiangsu 212001, China*

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Abstract

Bi_2WO_6 was modified by two-dimensional g-C_3N_4 (2D g-C_3N_4) *via* a hydrothermal method. The structure, morphology, optical and electronic properties were investigated by multiple techniques, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy spectra (XPS), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Ultraviolet-visible diffuse reflection spectroscopy (DRS), photocurrent and electrochemical impedance spectroscopy (EIS), electron spin resonance (ESR), respectively. Rhodamine B (RhB) was used as the target organic pollutant to research the photocatalytic performance of as-prepared composites. The Bi_2WO_6/2D g-C_3N_4 exhibited a remarkable improvement compared with the pure Bi_2WO_6. The enhanced photocatalytic activity was because the photogenerated electrons and holes can quickly separate by Z-Scheme passageway in composites. The photocatalytic mechanism was also researched in detail through ESR analysis.

Keywords: All-solid-state; Z-Scheme photocatalyst; 2D g-C_3N_4; Bi_2WO_6; Photocatalysis

1. Introduction

The increasing environmental pollution and energy crisis make it extremely urgent for human to develop green chemistry. In this instance, semiconductor photocatalysis, taking TiO_2 for example, has attracted much attention. However, TiO_2 is an ultraviolet-light-driven photocatalyst, which vastly limits its application. Although, many methods have been developed to increase the range of light absorption of TiO_2 to visible light, such as chemical doping with other elements (C-, N-, S-, *etc*), construction of composite structure with different semiconductors and preparing novel nanostructures, *etc* [1−4]. Nevertheless, the application of TiO_2 on photocatalysis is still limited due to the light response range and low quantum efficiency. On this background, new photocatalysts (such as g-C_3N_4 [5], CdS [6], Fe_2O_3 [7], Ag_3VO_4 [8], *ect*.) have been successfully synthesized and employed in photocatalytic fields.

Bismuth tungstate (Bi_2WO_6), known as one of the simplest Aruivillius oxides, has aroused much attention for its excellent properties in physics and chemistry acting as excellent photocatalytic and solar energy transfer materials [9,10]. Since Kudo and Hijii obtained Bi_2WO_6 successfully *via* solid state reaction [9], researchers have made much effort on preparing various structures of micro/nano-Bi_2WO_6, such as sol-gel and hydro/solvo-thermal method [11−15]. However, there are several disadvantages that limit the application of pure Bi_2WO_6, including low photo-absorption efficiency and high recombination of photo-induced electron and hole pairs. Based

* Corresponding authors.
E-mail addresses: jbmwgkc@126.com (M. He), lihm@ujs.edu.cn (H. Li).

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on this condition, modification strategies have being applied widely for the aim to enhance the photocatalytic performance of Bi_2WO_6. Chemical doping is one of the frequently-used approaches through doping metal and nonmetal (Ag, Mo, C, *etc*.) [16–19] to effectively extend the light responsive range and change the surface properties of materials. Besides, using co-catalyst or sensitizer [20–23] as reaction sites can also accelerate the interfacial charge transfer to enhance the photocatalytic activity. Specially, employing different semiconductor materials to generate heterojunction structure is a frequently-used method to couple with Bi_2WO_6 and thus improving the photocatalytic activity.

As a novel approach to further enhance the catalytic performance of bare photocatalysts, creating a Z-Scheme structure with another semiconductor which has suitable band position is considered as an efficient strategy. Except for the suppression of recombination of e^--h^+ pairs, Z-Scheme structure can also reserve high redox ability for both semiconductors. The graphite carbon nitride (g-C_3N_4) is chosen to be another component through modifying Bi_2WO_6 to develop a Z-Scheme system due to its suitable band structure, low cost and environmental friendliness as a metal-free material [24–31,33]. Recently, ultrathin two-dimensional (2D), especially monolayer materials have attached much attention in the field of photocatalysis for their excellent catalytic performance [34–40]. Compared with the bulk materials, 2D materials show larger surface areas for sufficient reactive sites, a shorter distance from the photogenerated electrons/holes to reaction interface and a probably larger bandgap [41,42]. Traditionally, liquid-phase exfoliation (LPE) was used for the preparation of few-layer and a small number of monolayer g-C_3N_4. However, it is difficult to remove the organic solvent left for the usage of exfoliation and stabilization, resulting in potential negative effect on photocatalytic activity [31,39,42]. On this background, monolayer g-C_3N_4 prepared *via* thermal oxidation was reported to have high crystallinity in a high yield and thus promoting photocatalytic efficiency [45].

In this work, 2D g-C_3N_4/Bi_2WO_6 composites were prepared successfully *via* hydrothermal method. The structures and morphologies of as-prepared samples were investigated by different characteristic measures. For photocatalytic performance, the 2D g-C_3N_4/Bi_2WO_6 Z-Scheme system exhibited giant enhancement in degrading Rhodamine B (RhB). The ESR analysis demonstrated the Z-Scheme mechanism in the photo-degradation process.

2. Experimental section

2.1. Preparation of photocatalysts

Bi_2WO_6 was synthesized through a hydrothermal process [43], in which 2.435 g $Bi(NO_3)_3 \cdot 5H_2O$ and 0.8246 g $Na_2WO_4 \cdot 2H_2O$ were dissolved in 100 mL deionized water. An ultrasonic process was taken for 20 min before the suspension transferred into a 25 mL Teflon-lined autoclave. After heated at 160 °C for 12 h, the precipitate was then cooled down to the room temperature and washed with distilled water and ethanol. Finally, the samples were dried at 80 °C for 8 h to collect the final products. The 2D g-C_3N_4 was prepared by the method in the literatures [41]. Firstly, the bulk g-C_3N_4 was prepared by directly heating melamine at 550 °C for 4 h. The yellow powder sample was again heated at 550 °C for twice. The obtained white sample was denoted as 2D g-C_3N_4.

2D g-C_3N_4/Bi_2WO_6 hybrid photocatalysts were assembled by hydrothermal synthesis and labeled as x% for convenience (x represents wt% of 2D g-C_3N_4 in Bi_2WO_6). The 15% 2D g-C_3N_4/Bi_2WO_6 composite was obtained as follows: 7.5 mg 2D g-C_3N_4 and 50 mg Bi_2WO_6 were dissolved in 20 mL deionized water. After ultrasonic agitation and stirred for about 30 min, the slurry solution was transferred into a 25 mL Teflon-lined autoclave and heated at 150 °C for 4 h. The obtained sample was then washed with water for several times and dried at last. The other scales of composites were synthesized similarly.

2.2. Characterization

X-ray diffraction (XRD) was used to investigate the crystal structure of the as-prepared samples by a Shimadzu XRD-6000 X-ray diffractomter (Cu Kα source), which the range of 2θ was from 10° to 80° with a scan rate of 7°/min. The Fourier transform (FT-IR) spectra were obtained by a Nicolet Nexus 470 with KBr disk at the room temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250XI electron spectrometer. The scanning electron microscopy (SEM) was taken into practice with a field-emission scanning electron microscope ([JEOL-JSM-7001F]), equipping with an energy-dispersive X-ray spectroscope (EDS). Transmission electron microscopy (TEM) was carried out with a transmission electron microscope (JEOL-JEM-2010) at an acceleration voltage of 200 kV. Ultraviolet-visible (UV-vis) diffuse reflection spectra (DRS) were measured using a spectrophotometer (Shimadzu UV-2450) with $BaSO_4$ as reference at the range of 200–800 nm. The photocurrent and electrochemical impedance spectroscopy (EIS) were measured on an electrochemical impedance station (CHI 660B Chenhua Instrument Company). The PL spectra were collected with a Varian Cary Eclipse spectrometer. The electron spin resonance (ESR) signals were collected by spin-trap reagent DMPO (Sigma Chemical Co.) in water using a Bruker model ESR-JES-FA200 spectrometer.

2.3. Photocatalytic activity

In order to investigate the photocatalytic activity of as-prepared samples, Rhodamine B (RhB) was degraded as the model pollute, using a 250 W Xe lamp with a 400 nm cutoff filter. In each photodegradation process, 0.02 g photocatalyst were dissolved into 50 mL RhB (10 mg/L) and reacted in a Pyrex photocatalytic reactor, which was connected to a circulating water system to keep the reaction temperature at 30°C during the whole degradation process. Prior to irradiation, to ensure the RhB reaching the absorption-desorption

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