Materials Research Bulletin 83 (2016) 172–178

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Mixed-calcination synthesis of Bi_2MoO_6/g-C_3N_4 heterojunction with enhanced visible-light-responsive photoreactivity for RhB degradation and photocurrent generation

Ke Xiao, Hongwei Huang*, Na Tian, Yihe Zhang*

Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

ARTICLE INFO

Article history:
Received 20 February 2016
Received in revised form 2 May 2016
Accepted 14 May 2016
Available online 16 May 2016

Keywords:
A. layered compounds
A. semiconductors
B. chemical synthesis
C. impedance spectroscopy
D. catalytic properties

ABSTRACT

Organic-inorganic hybrid photocatalyst Bi_2MoO_6/g-C_3N_4 was synthesized via a mixed-calcination route based on intimate interfacial interaction. The successful combination of g-C_3N_4 and Bi_2MoO_6 was verified by X-ray diffraction (XRD), Fourier-transform infrared spectra (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) mapping. The optical property of the as-prepared photocatalysts was characterized by UV–vis diffuse reflectance spectra (DRS). The photocatalytic activities were investigated by degradation of Rhodamine B (RhB) and photocurrent generation under visible-light ($\lambda > 420$ nm). The results demonstrated that the Bi_2MoO_6/g-C_3N_4 composite exhibits highly enhanced photoreactivity compared to the pristine samples. It should be attributed to the fabrication of a Bi_2MoO_6/g-C_3N_4 heterojunction, thus resulting in the high separation and transfer efficiency of photogenerated charge carriers, as confirmed by the photoluminescence (PL) and electrochemical impedance spectra (EIS). The active species trapping experiments indicated that holes (h^+) and superoxide radicals ($^{\bullet}O_2^-$) are the main active species in the degradation process.

1. Introduction

Nowadays, the problems on environmental deterioration and energy shortage have been bothering people, and green chemistry has become a necessary requirement for the sustainable development of human society. Among the various green techniques, semiconductor photocatalysis has emerged as one of the most promising technologies because the semiconductor photocatalyst can use the solar energy for degradation of organic contaminants [1–3]. In order to achieve the above goals, two problems must be resolved, increasing the separation efficiency of photoexcited electron-hole pairs and extending the excitation wavelength range of photocatalysts. To extend the absorption-wavelength range, the semiconductor materials, such as oxides, sulfides and nitrides etc., which can be excited by visible light, have been investigated extensively. However, a single-phase photocatalyst exhibits significant limitations in the process of photocatalytic reactions due to the quick combination of photogenerated electrons and holes. To enhance the separation efficiency of photoexcited charge carriers, fabrication of heterojunction photocatalysts have been extensively investigated [4,5].

Recently, a polymer photocatalyst named graphitic carbon nitride (g-C_3N_4) has attracted intensive attention for hydrogen gas evolution via water splitting, photocatalytic degradation of organic pollutants and photosynthesis under visible light illuminat ion [6–8]. It is known that the band gap of g-C_3N_4 is about 2.7 eV, which can absorb visible light with wavelength up to 459 nm. Furthermore, the conduction band (CB) minimum (−1.13 eV vs. NHE) of g-C_3N_4 is extremely negative, so photogenerated electrons should have a strong reduction ability. However, the photocatalytic efficiency of single g-C_3N_4 is limited due to the insufficient visible-light absorption and high recombination probability of photoexcited electron-hole pairs. In order to improve the photocatalytic activity of g-C_3N_4, many strategies such as doping and coupling with other semiconductor materials have been used to modify g-C_3N_4 [9,10].

Bismuth molybdate compounds are a kind of important catalyst materials, which have been widely used in the preparation of selective oxidation of propylene dehydrogenation propylene aldehydes, propylene ammoxidation preparation nitrile, etc. In addition, these compounds can also serve as ion conductor, audio and video materials, optical conductor and gas sensor due to its

---

* Corresponding authors.
E-mail addresses: hhw@cugb.edu.cn (H. Huang), zyh@cugb.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.materresbull.2016.05.016
0025-5408/

unique physical properties. Recent studies have shown that Bi_2MoO_6 possesses excellent visible light photocatalytic properties [11,12]. Its crystal structure consists of alternating $[Bi_2O_2]^{2+}$ layers and MoO_6 octahedral perovskite layers. It has been reported that in the crystal structure of a layered compound, the separation and migration of charge carrier are much easier, thus resulting in high photocatalytic activity [13,14]. Recently, Li et al. reported the synthesis of g-C_3N_4/Bi_2MoO_6 composites by a solvothermal method [15]. However, the above composites may fail to achieve controllable compositing degree and strong interfacial interaction.

In this work, we successfully prepared the heterostructural photocatalyst of Bi_2MoO_6/g-C_3N_4 by a mixed-calcination method, which may provide a more reliable interfacial interaction between g-C_3N_4 and Bi_2MoO_6. The photocatalytic activity of the Bi_2MoO_6/g-C_3N_4 was evaluated by decomposing RhB and photocurrent generation under visible light irradiation ($\lambda > 420$ nm). The Bi_2MoO_6/g-C_3N_4 composite exhibits superior RhB photodegradation rate and photocurrent response, which should be attributed the efficient separation of photoinduced charge carriers originated from the Bi_2MoO_6/g-C_3N_4 heterojunction fabrication. The structure, optical property and photocatalytic mechanism of the as-prepared photocatalysts are investigated in details.

2. Experimental

2.1. Synthesis of heterostructured Bi_2MoO_6/g-C_3N_4 photocatalyst

All chemicals were used in analytical grade without further purification. The g-C_3N_4 precursor was synthesized through pyrolysis of melamine in a crucible without a cover under ambient pressure in air [16]. The details are as follows: The melamine was added in a crucible and heated to 520 °C at a heating rate of 3 °C min^{-1} in a tube furnace for 4 h. After cooling to room temperature, the yellow product was collected and milled into powder.

Pure Bi_2MoO_6 was prepared by hydrothermal method: Firstly, 0.004 mol of $Na_2MoO_4 \cdot 2H_2O$ was totally dissolved in 25 mL of distilled water to form solution A. Secondly, 0.008 mol of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in the A solution. Then, the resultant mixture was sealed in a 50 mL Teflon-lined stainless steel autoclave, and heated and maintained at 180 °C for 12 h, then cooling to room temperature. After funnel separation, the powder was washed with water for several times and then dried at 80 °C in a vacuum oven.

The Bi_2MoO_6/g-C_3N_4 composites were prepared through a mixed-calcination method at 400 °C. 0.0005 mol g-C_3N_4 and 0.0015 mol Bi_2MoO_6 were both dissolved in 50 mL of ethanol under ultrasonic oscillation for 1 h, and then dried in the oven at 60 °C. The mixed powder was collected and calcined at 400 °C for 0.5 h to obtain the 1:3 Bi_2MoO_6/g-C_3N_4 photocatalyst. Other Bi_2MoO_6/g-C_3N_4 photocatalysts with the molar ratio of 1:5, 1:1 and 3:1 were prepared by the same method.

2.2. Characterization

The phase structures of photocatalysts were investigated by X-ray powder diffraction (XRD) analysis at room temperature on an XRD powder diffraction instrument with monochromatized Cu Kα radiation ($\lambda = 1.5406$ nm) at a setting of 40 kV and 40 mA. And the Scanning rate and range were 0.02° (2θ)/s and 10–70°, respectively. Fourier-transform infrared (FTIR) spectra were obtained using a Bruker spectrometer in the frequency range of 4000–500 cm^{-1}. The morphologies and microstructures of the photocatalysts were studied by field emission scanning electron microscopy (SEM) (Hitachi S-4800). UV–vis diffuse reflectance spectra (DRS) were recorded on a Cary 5000 (America Varian) spectrophotometer. The photoluminescence (PL) spectra of the samples were measured using a Hitachi F-4600 fluorescence spectrophotometer to observe the combination rate of electron-hole pairs.

2.3. Photocatalytic activity measurements

The photocatalytic activities of the samples were evaluated by the degradation of the RhB under visible light irradiation (300 W xenon lamp, $\lambda > 420$ nm). 50 mg of the as-prepared photocatalyst was dispersed into 50 mL of RhB solution (1×10^{-5} mol/L). Prior to illumination, the adsorption-desorption equilibrium between photocatalyst powder and RhB was obtained by vigorously stirred for 1 h min. And then, the light was turned on, and 2 mL of the suspensions were taken into the centrifuge tubes at selected intervals. The vigorously stirring was maintained throughout the whole reaction process. After that, the photocatalysts in the mixture were removed by centrifugation (4500 r/min, 5 min) and the centrifuged solution was analyzed by recording the maximum absorption band (554 nm for RhB) and UV–vis spectra were recorded by Shimadzu UV-5500PC spectrophotometer (Shanghai Wuxiang Company).

2.4. Active species trapping experiments

The active species, such as hydroxyl radicals ($^{\bullet}OH$), superoxide radical ($^{\bullet}O_2^-$) and holes (h^+) were detected by adding isopropyl

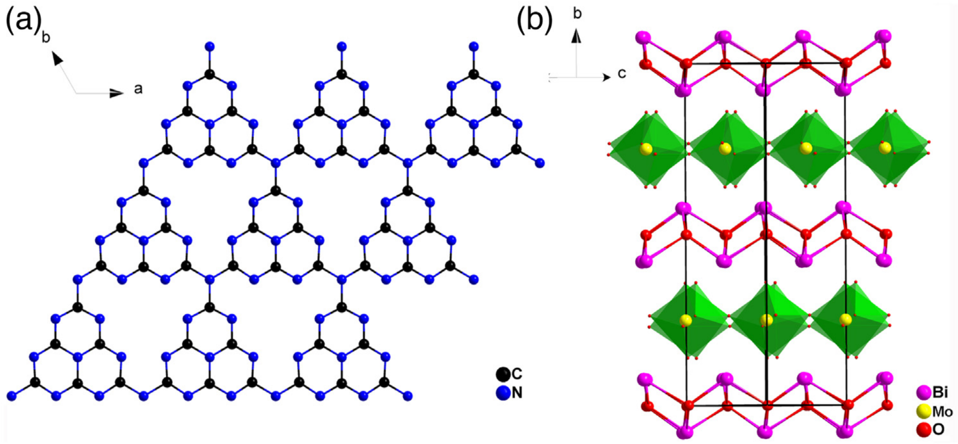

Fig. 1. Crystal structures of g-C_3N_4 and Bi_2MoO_6.