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Low-heating solid-state chemical synthesis of monoclinic scheelite $BiVO_4$ with different morphologies and their enhanced photocatalytic property under visible light

Zhiting Liang, Yali Cao*, Haiyu Qin, Dianzeng Jia*

Key Laboratory of Energy Materials Chemistry, Ministry of Education, Key Laboratory of Advanced Functional Materials, Autonomous Region, Institute of Applied Chemistry, Xinjiang University, Urumqi, Xinjiang 830046, China

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ABSTRACT

The monoclinic scheelite $BiVO_4$ with different morphologies were synthesized by low-heating solid-state chemical reaction method without template or organic surfactant. The addition of weak base $NaHCO_3$ can change the morphology of $BiVO_4$ from polyhedrons to peanut-like and rice-like shape because that the base changed the microenvironment of the reaction system, increased the nucleation rate of product and hindered the further growth of the original product particle in process of solid-state reaction. Among the as-fabricated $BiVO_4$ samples, the rice-like sample showed the best photocatalytic activity of 98.2% degradation for methylene blue solution after irradiation of 2 h under visible light, which attributed to the efficient separation of photoexcited electrons and holes that improved the quantum efficiency during the photodegradation process. With the help of scavengers, $^{\bullet}OH$ and $^{\bullet}O^{2-}$ were proved to be the main reactive species for the degradation of methylene blue.

1. Introduction

Semiconductor photocatalytic technology has been regard as an ideal candidate to deal with energy and environmental problems. Over the past decades of years, TiO_2 has been successfully applied to eliminate the hazardous contaminants in water [1,2]. However, TiO_2 only utilized UV light because of its wide band gap (3.2 eV) and restricted its practical application [3]. To take full advantage of large fraction of visible light (48%) in the solar spectrum for energy conversion, it is desirable to explore the visible light responsive photocatalysts. Up to now, many photocatalysts driven by visible light have been extensively studied, such as Ag_3PO_4 [4], Bi_2WO_6 [5], Bi_2MoO_6 [6], $BiVO_4$ [7] and so on. Among them, $BiVO_4$ has drawn much attention due to its high efficiency and good stability since its first reported for O_2 evolution under visible light irradiation by Kudo et al. [8].

As is known, $BiVO_4$ has three crystalline phase forms: tetragonal zircon (z-t), tetragonal scheelite (s-t) and monoclinic scheelite (m-s). Monoclinic scheelite $BiVO_4$ has attracted extensive attention in photocatalysis because of its narrow band gap (2.4 eV), low toxicity and excellent visible-light responsive ability in past years [9,10]. Recently, some methods, such as hydrothermal or solvothermal syhthesis [11,12], sol-gel process [13], co-precipitation strategy [14] and sonochemical method [15] have been employed to prepare $BiVO_4$ nanocrystallites with different morphology that have excellent photocatalytic property. These methods have limit of solubility for reactant in the design of chemical reaction system, and used organic additives or surfactants in the synthetic process [16,17], which not only increased production costs but also brought organic pollutants. Therefore, it still remains a significant challenge to develop facile, non-solvent and effective additive-free methods for the controlled synthesis of $BiVO_4$ photocatalyst with desired morphology.

Solid-state chemical reaction synthesis has advantages of convenient operation, low cost and less pollution. Especially, compared with the liquid phase synthesis, solid-state chemical reaction synthesis has no limit of solubility for reactants in designing the experimental reaction program. In the past years, various nanomaterials have been prepared by the low-heating or room-temperature solid-state chemical reaction in our research group [18–22]. In this paper, we fabricated monoclinic $BiVO_4$ with different morphologies by low-heating solid-state chemical reaction method without any surfactants or organic reagent. Their excellent photocatalytic properties have been investigated.

* Corresponding authors.
E-mail addresses: caoyali@xju.edu.cn (Y. Cao), jdz@xju.edu.cn (D. Jia).

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2. Experimental

2.1. Preparation of photocatalysts

In a typical synthesis, 10 mmol of solid $Bi(NO_3)_3{\cdot}5H_2O$ was accurately weighed and grounded for about 5 min in agate mortar, then was added 10 mmol of solid $NaVO_3$ power, the ultrafine yellow mixture was obtained. After continually ground for 5 min, certain amount $NaHCO_3$ (0.2 g, 0.4 g, 0.6 g) was added into the above yellow mixture, then constantly ground about 30 min. The mixture were oil bath heated at 120 °C for 24 h, then washed with deionized water for several times to remove by-product, the yellow $BiVO_4$ samples were finally synthesized. The achieved $BiVO_4$ samples named as BVO-2, BVO-3 and BVO-4 according to the $NaHCO_3$ amount of 0.2 g, 0.4 g and 0.6 g, respectively. As a reference sample, another $BiVO_4$ was also prepared using the same procedure as BVO-2 without the addition of $NaHCO_3$ and designated as BVO-1. Fig. 1 showed the complete fabrication procedures of the $BiVO_4$ samples.

2.2. Characterization of photocatalysts

The products were characterized by X-ray diffraction (XRD) on Bruker D8 X-ray diffractometer with Cu-Kα radiation (λ = 1.54056 Å) ranging from 10° to 60°. Morphologies of the prepared samples were further examined by field emission scanning electron microscopy (FESEM, Hitachi S-4800 at 5 kV). UV–vis diffuse reflectance spectra (DRS) and UV–vis absorption spectra of the samples were measured using UV–vis spectrophotometer (Hitachi U-3010 and U-3900), using $BaSO_4$ as a reflectance standard. The surface area and porosity analyzer were obtained on a Micromeritics ASAP 2020 by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halender (BJH) method. The photocatalytic experiments were conducted in an XPA-1 photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China). The photoluminescence (PL) spectra of as-fabricated products were collected through fluorescence spectrophotometer (Hitachi F-4500). The photocurrent was carried out on an electrochemical system (CHI-660D, China).

2.3. Photocatalytic degradation experiment of photocatalysts

Photocatalyitc activities of as-fabricated $BiVO_4$ samples were evaluated by the degradation of methylene blue (MB) as a model reaction under visible light irradiation using a 350 W Xe lamp with a 420 nm cutoff filter. A water-cooling system was applied to maintain the reaction temperature at room temperature and the constant stir was maintained to keep the mixture in suspension. Firstly, 20 mg as-prepared samples were ultrasound-dispersed in an aqueous solution of 50 mL MB (10 mg L^{-1}). Then, the mixed solution was magnetically stirred in dark for more than one hour to get absorption/desorption equilibrium of MB with the catalyst. Subsequently, the suspension was exposed to the visible illumination and continuously agitated throughout the experiment. At certain irradiation time intervals, 4 mL of the suspension was taken out and centrifuged to remove the catalyst. The concentration of MB was determined by measuring the UV–vis absorption at the maximum absorption wavelength of 664 nm. The photocatalytic degradation ratio was calculated by the following formula.

$$\text{Degradation ratio} = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

Where $C_0$is the initial concention of MB and C_t is the MB concention of different irradiation times *t*.

2.4. Photo-electrochemical measurement of photocatalysts

The photocurrent measurement was measured on an electrochemical system (CHI-660D, China). The fabrication of photoanode for our products was fabricated as follows. 1 mL of ethanol and 10 mg of as-prepared photocatalyst was mixed homogeneously, then the homogeneous mixture was spread on the indium tin oxide (ITO) conducting glass, the exposed area under illumination was 0.2 cm^2. The films were dried in a vacuum oven at 60 °C for 10 h, then they were sintered in air at 150 °C for 5 h. The photocurrent measurement was conducted with a standard three-electrode: a working electrode (as-prepared photocatalyst films on ITO conducting glass), a platinum wire as counter electrode, and a standard calomel electrode (SCE) as reference electrode. 0.5 M Na_2SO_4 was used as the electrolyte solution. The 350 W Xe lamp with a 420 nm cutoff filter was used as light source.

3. Results and discussion

3.1. Structure and optical absorption behavior of photocatalysts

A typical XRD pattern of the as-prepared samples are presented in Fig. 2. It can be seen that all the peaks are well assigned to the pure monoclinic scheelite $BiVO_4$ (JCPDS No. 14-0688). No impure phases are observed in all XRD patterns. It is apparent that the crystallized monoclinic $BiVO_4$ product can be easily obtained by the solid-state strategy. The peaks in 2θ = 18.5° and 18.7° for sample BVO-1 prepared without $NaHCO_3$, corresponding to the (110) and (011) peaks are obviously observed. The two peaks merge into one peak due to the peak broaden for BVO-2, BVO-3 and BVO-4 that were prepared by the addition of $NaHCO_3$. The observation indicates that $NaHCO_3$ may change the alkalinity of reaction system, result the decreased size of the products. This can be directly observed in following SEM.

The optical absorption property has a relationship with its energy band gap, which plays a crucial role in its photocatalytic activity. The photoabsorption property of the samples can be tested by UV–vis diffuse reflectance spectra. Fig. 3(a) exhibited the UV–vis diffuse reflectance spectra. According to the spectrum, all the samples showed a broad absorption in the visible region, indicating promising photocatalytic activity under visible light. Energy band gaps (E_g) of a semiconductor is related to its absorption property, which can be calculate in accordance with the reported equation [23]:

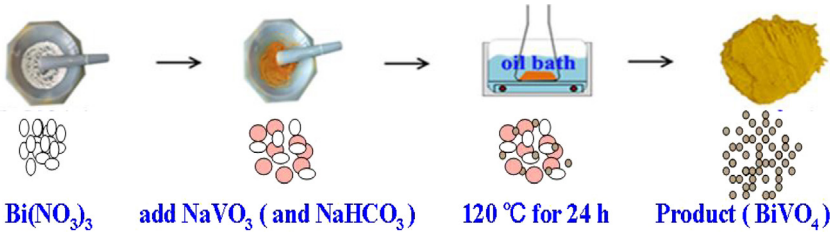

Fig. 1. Schematic of the fabrication procedures for $BiVO_4$ samples.