Journal of Hazardous Materials 173 (2010) 194–199

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

CTAB-assisted synthesis of monoclinic $BiVO_4$ photocatalyst and its highly efficient degradation of organic dye under visible-light irradiation

Wenzong Yin, Wenzhong Wang*, Lin Zhou, Songmei Sun, Ling Zhang

State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, PR China

ARTICLE INFO

Article history:
Received 11 March 2009
Received in revised form 11 August 2009
Accepted 16 August 2009
Available online 22 August 2009

Keywords:
Monoclinic $BiVO_4$
Photocatalyst
CTAB
De-ethylation
Conjugated chromophore structure

ABSTRACT

A highly efficient monoclinic $BiVO_4$ photocatalyst (C-BVO) was synthesized by an aqueous method with the assistance of cetyltrimethylammonium bromide (CTAB). The structure, morphology and photophysical properties of the C-BVO were characterized by XRD, FE-SEM and diffuse reflectance spectroscopy, respectively. The photocatalytic efficiencies were evaluated by the degradation of rhodamine B (RhB) under visible-light irradiation, revealing that the degradation rate over the C-BVO was much higher than that over the reference $BiVO_4$ prepared by aqueous method and over the one prepared by solid-state reaction. The efficiency of de-ethylation and that of the cleavage of conjugated chromophore structure were investigated, respectively. The chemical oxygen demand (COD) values of the RhB were measured after the photocatalytic degradation over the C-BVO and demonstrated a 53% decrease in COD. The effects of CTAB on the synthesis of C-BVO were investigated, which revealed that CTAB not only changed the reaction process via the formation of BiOBr as an intermediate, but also facilitated the transition from BiOBr to $BiVO_4$. Comparison experiments were carried out and showed that the existence of impurity level makes significant contribution to the high photocatalytic efficiency of the C-BVO.

1. Introduction

Organic dyes in textile and other industrial effluents have become one type of the major environmental contaminants. As many dyes are highly water-soluble, traditional treatment methods including flocculation, activated carbon adsorption, and biological treatment do not work efficiently [1]. Recently, photocatalysis method has played an important role in the degradation of organic dyes in wastewater [2,3]. Compared with other treatment, photocatalytic degradation has several advantages, such as the use of environmentally friendly oxidant O_2, complete mineralization, no waste disposal problem, and a necessity of only mild temperature and pressure conditions [3,4]. Moreover, the photocatalytic degradation is able to work out even at a much low concentration of organic dyes. Therefore, photocatalytic degradation is a promising solution to organic dyes. Early studies on photocatalysts mainly focused on the Ultraviolet-driven TiO_2 photocatalyst [5–7]. However, UV light takes up only *ca.* 4% of the solar energy while visible-light *ca.* 43%. Hereby, visible-light-driven photocatalysts have been the new focus [8–10].

Since $BiVO_4$ was found to be an active photocatalyst for O_2 evolution from aqueous $AgNO_3$ solution under visible-light irradiation [11], more and more attention has been attracted to the synthesis of visible-light-driven $BiVO_4$ photocatalyst. Among the three crystalline phases of $BiVO_4$, tetragonal zircon (z-t), tetragonal scheelite (s-t) and monoclinic scheelite (s-m) structures [12], it is found that the monoclinic scheelite $BiVO_4$ (m-$BiVO_4$) exhibits much higher photocatalytic activity than the other two tetragonal phases [13,14]. Therefore, many methods have been employed for the synthesis of m-$BiVO_4$, such as solid-state reaction [15,16], hydrothermal or solvothermal method [17–21], aqueous method [22–24], ultrasound- or microwave-assisted route [25,26], metal-organic decomposition [27,28], flame spray pyrolysis [29], and solution combustion method [30]. Compared with other methods, aqueous method provides a milder environment for the synthesis of monoclinic $BiVO_4$ and the reaction parameters as well as the properties of the products could be easily tuned. To the best of our knowledge, however, the synthesis of $BiVO_4$ by aqueous method with the assistance of CTAB has not been reported.

In the present study, highly efficient m-$BiVO_4$ photocatalyst was synthesized by a CTAB-assisted aqueous method and rhodamine B (RhB) was used as a model dye to evaluate its photocatalytic efficiency under visible-light irradiation. Furthermore, the efficiencies both in de-ethylation and cleavage of chromophore structure were investigated, respectively. The 53% decrease of the COD values for the RhB solutions after the irradiation confirmed the photocatalytic degradation of RhB. The effects of CTAB addition on the products

---

* Corresponding author. Tel.: +86 21 5241 5295; fax: +86 21 5241 3122.
E-mail address: wzwang@mail.sic.ac.cn (W. Wang).

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.08.068

Table 1
List of the samples prepared in different conditions.

	C-BVO	C-BVO-cal	NC-BVO	SSR-BVO	AM-BVO
CTAB	Y	Y	N	Ref. [15]	Ref. [8], [23]
Calcination	N	Y	N		

were investigated. Possible reasons for the enhanced efficiencies of m-BiVO$_4$ photocatalyst were discussed.

2. Experimental

2.1. Synthesis

All the reagents were of analytical purity from Shanghai Chemical Company and used without further purification. In a typical procedure, 2 mmol of NH_4VO_3 was first dissolved into 20 mL of de-ionized water at 96 °C and then the solution was cooled to room temperature. The NH_4VO_3 solution was added dropwise into a 250 mL flask containing 40 mL of CTAB solution (0.05 M) in an oil bath at 60 °C. Afterwards, 2 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ was added into 20 mL of de-ionized water and stirred for about 10 min to form a hydrolyzed white floccule. The floccule suspension was added dropwise into the flask at 60 °C under stirring. After that, the flask was connected with a condenser and heated in oil bath at 80 °C for 12 h. The final product was centrifuged, washed with de-ionized water and absolute ethanol for several times, and dried in air. The as-prepared m-BiVO$_4$ crystals were denoted as C-BVO. For comparison, m-BiVO$_4$ crystals were also synthesized by solid-state reaction (SSR-BVO) according to Ref. [15] and by aqueous method (AM-BVO) as reported in Ref. [8] and [23]. The major samples prepared in our experiment were denoted and listed in Table 1.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the samples were measured with a Rigaku D/Max-2200PC diffractometer using monochromatized Cu Kα radiation ($\lambda = 0.15418$ nm) at a scanning rate of 8°/min. The field emission scanning electron microscope (FE-SEM) images were obtained on a JEOL JSM-6700F field emission scanning electron microscope. The diffuse reflectance spectra (DRS) of the $BiVO_4$ samples and the UV–vis absorption spectra of the RhB solutions were obtained on a Hitachi U-3010 UV–vis spectrophotometer.

2.3. Photocatalytic efficiency

RhB shows a major absorption band centered at 553 nm which is used to monitor the photocatalytic degradation of RhB. The photocatalytic efficiencies of the $BiVO_4$ were evaluated by the degradation of RhB under visible-light irradiation. The visible-light irradiation was provided by a 500 W Xenon lamp (Shanghai Yaming Lighting Co. Ltd.) with a 420 nm cutoff filter. Each experiment was performed at room temperature as follows: 0.1 g of $BiVO_4$ photocatalyst was added into 100 mL of RhB solution with a concentration of 10^{-5} M. Before illumination, the suspension was stirred in the dark for 12 h to ensure adsorption/desorption equilibrium between RhB and the photocatalyst. Then the suspension was stirred and exposed to visible-light irradiation. At given time intervals, 2 mL of the suspensions was taken out and centrifuged to remove the photocatalyst particles. The concentrations of the centrifuged RhB solutions were monitored using a Hitachi U-3010 UV–vis spectrophotometer. Chemical oxygen demand (COD) measurements were carried out by the dichromate titration method [31] on the RhB solutions before and after 8 h of visible-light irradiation over 0.2 g of the C-BVO. The initial concentration of the RhB solution is 2×10^{-4} M.

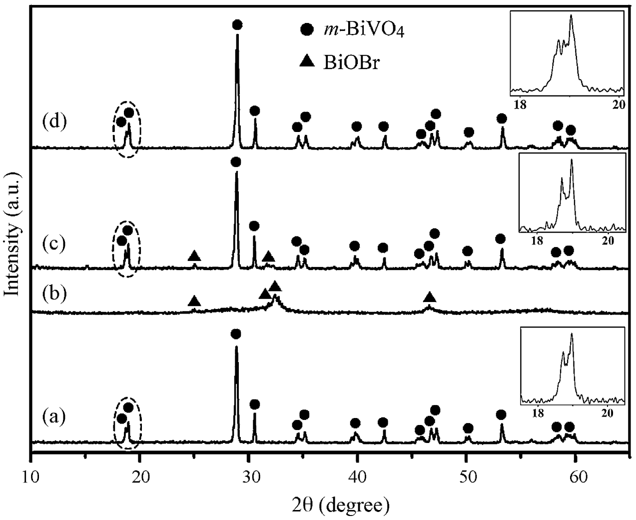

Fig. 1. XRD patterns of the C-BVO (a), the products prepared by CTAB-assisted aqueous method at 80 °C for 3 h (b) and 6 h (c), and the C-BVO-cal (d). Inset: the widened parts of XRD patterns near 19°, showing the characteristic split of monoclinic $BiVO_4$.

3. Results and discussion

3.1. Characterization of the C-BVO

Fig. 1a shows the XRD pattern of the C-BVO. All the diffraction peaks can be indexed to m-BiVO$_4$ which is identical to the standard (JCPDS no. 14-0688). Characteristic splitting of peaks at 18.5°, 35°, and 46° of 2θ is observed for m-BiVO$_4$. The sharp and narrow diffraction peaks indicate a high crystallinity of the m-BiVO$_4$. No diffraction peaks of other phases are detected.

Fig. 2 shows the SEM images of the C-BVO. The shapes of the C-BVO particles are nearly spherical. The sizes of these particles range from 400 nm to 700 nm. Magnified image in Fig. 2b shows a rough surface of the C-BVO particles.

The diffuse reflectance spectrum (DRS) of the C-BVO is shown in Fig. 3a. It is obvious that the absorption edge of the DRS curve possesses an elongated tail, which suggests the formation of surface states and impurity levels [13].

3.2. Photocatalytic efficiency of the C-BVO

The characteristic absorption of RhB which lies at the wavelength of 553 nm has been used to monitor the photocatalytic degradation process. Fig. 4 represents the decrease of RhB (C/C_0) as a function of irradiation time without photocatalyst and over the C-BVO, AM-BVO and SSR-BVO. Here, C is the absorption of RhB at the wavelength of 553 nm and C_0 is the absorption of RhB after the adsorption equilibrium on $BiVO_4$ photocatalysts before irradiation. The photolysis of RhB under visible-light irradiation is neglectable (Fig. 4d), as reported in Ref. [17]. RhB is almost completely degraded after 20 min of irradiation over the C-BVO under visible-light (Fig. 4a). However, only about 12.5% of RhB can be degraded over the SSR-BVO and 85% over the AM-BVO after 120 min of irradiation (Fig. 4b and c). According to Ref. [32], the RhB degradation over the photocatalysts is fitted for pseudo-first-order kinetics and the reaction constant k, which was used to evaluate the degradation rate, could be determined by the plots of $\ln(C/C_0)$ vs irradiation time (t). The determined k values for the C-BVO, AM-BVO and SSR-BVO are 0.233(±0.008), $1.805(\pm 0.079) \times 10^{-2}$, and $8.268(\pm 0.113) \times 10^{-4}$ min^{-1}, respectively. Their linearly dependent coefficients (R) are 0.998, 0.996 and 1.000, respectively, indicating a good linear dependence relation. It is clear that the k value for the C-BVO is about 12 times higher than that for the AM-