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Short communication

Controllable synthesis and photocatalytic activity of spherical, flower-like and nanofibrous bismuth tungstates

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ABSTRACT

Highly crystalline Bi_2WO_6 particles with high visible light photocatalytic activity were controllably synthesized via a facile hydrothermal process. The phase structures and morphologies were measured by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). XRD patterns demonstrated that the as-prepared Bi_2WO_6 samples were orthorhombic cell. FESEM showed that Bi_2WO_6 crystals with distinctive morphologies could be selectively obtained by adjusting the reaction parameters of the hydrothermal process. The formation mechanisms of these distinctive structures were then discussed based on the morphologies analysis of the samples prepared at different conditions. The flower-like Bi_2WO_6 nanosturcture showed higher photocatalytic activity than that of nanofibrous and spherical Bi_2WO_6 under visible light irradiation ($\lambda > 420$ nm). The reason for the difference in the photocatalytic activities for the three representative samples was systematically studied based on their shape, size and specific surface area.

1. Introduction

Semiconductor photocatalysts have attracted increasing attentions for their applications in solar energy conversion and environmental remediation [1]. During the past several decades, the thoroughly studied conventional TiO_2 has displayed excellent activities and stabilities [2–4]. However, the deficiency of requiring UV light for effective photocatalysis severely hinders the overall process to be used in practical. Therefore, the development of visible light responsive photocatalysts has become one of imperative topics in current photocatalysis research [5–11].

Bi_2WO_6 is the simplest member of the Aurivillius family (when $n = 1$) with general formula $Bi_2A_{n-1}B_nO_{3n+3}$ (A = Ca, Sr, Ba, Pb, Bi, Na, K and B = Ti, Nb, Ta, Mo, W, Fe), which usually have the layer structures and unique properties [5,6,12–14]. Recent years, Bi_2WO_6 has attracted extensive attentions due to its excellent intrinsic physical and chemical properties such as ferroelectric piezoelectricity, catalytic behavior, and nonlinear dielectric susceptibility [15,16]. More importantly, it has been found that Bi_2WO_6 exhibits the highest photocatalytic activity among the above Bi^{3+}-based oxides under visible light irradiation. In order to confirm its photocatalytic activity, Kudo and Hijii [17] employed it to photocatalytically produce oxygen from water. Wang and Zhang et al. have also reported that Bi_2WO_6 and its based photocatalysts can effectively degrade organic pollutants and/or disinfect the bacteria under visible light irradiation [18–23].

As we all know, the properties of materials with the same composition but different morphologies could be substantially different. Therefore, the better performance of material is not only depended on the compositions but also on the morphologies of the materials. The dependence of the properties of nanomaterials on both the size and shape is a phenomenon of both fundamental scientific interest and many practical and technological applications [16]. In order to advance the basic understanding of the principles that determine the shape and to provide tailored building blocks for nanodevices, many efforts have been made to control the shape, dimensionality, and assembly of nanostructures [24–26]. As known, both the size and the morphology have an influence on the properties of semiconductor oxides. For example, nanoscale photocatalysts are believed to perform better than the bulk materials due to the higher surface-to-volume ratio and separation efficiency of the photogenerated electrons and holes [27]. Thus, morphology control provides a greater versatility for tuning the photocatalytic properties of semiconductor materials. It should be noted that the

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photocatalytic performances of Bi_2WO_6 based photocatalysts are seriously dependent on their particle size, structure, crystallization degree and composition [18–23]. Researches have reported the photocatalytic property of Bi_2WO_6 depending on the morphology for decomposition of rhodamine B: Tian et al. [28] have discussed the photocatalytic performances of Bi_2WO_6 with different morphologies (the caddice clew-like, flower-like and nest-like Bi_2WO_6 hierarchical nano/microstructures). Huang et al. [29] have reported the photocatalytic activity of various morphologies of Bi_2WO_6 including coralloid spherical particles, packed nanosheets, fluffy microspheres, and plates.

In this work, we report a simple hydrothermal method for the successful synthesis of Bi_2WO_6 crystals with well controlled shapes. The influence of reaction parameter on the Bi_2WO_6 morphology, structure and the relationship between the morphology and photocatalytic activities were investigated. The aim of this research was to develop a method for the fabrication of different-dimensional Bi_2WO_6 nanomaterials and to adjust the properties by modulating the morphology and size of the materials.

2. Experimental

2.1. Preparation of Bi_2WO_6 photocatalysts

All reagents used in our experiment were of analytical purity and used without further purification. The Bi_2WO_6 samples with different morphologies were fabricated by adopting the hydrothermal strategy with $Bi(NO_3)_3{\cdot}5H_2O$ and $Na_2WO_4{\cdot}2H_2O$ as metal source in the absence and presence of surfactant sodium dodecyl benzene sulfonate (SDBS). The typical fabrication procedure is as follows: under stirring conditions, 0.03 g or 0.06 g of SDBS and 1.3582 g of $Bi(NO_3)_3{\cdot}5H_2O$ powders were added to a 250 mL beaker containing 10 mL of acetic acid aqueous solution (36 wt%) and 10 mL of deionized H_2O. After being well mixed, 0.4619 g of $Na_2WO_4{\cdot}2H_2O$ powders was added to the above mixed solution. The amorphous yellow slurry formed immediately. A certain amount of an alkaline (i.e., $NH_3{\cdot}H_2O$ (14 wt%) solution) source was added to adjust the pH value of the above mixed solution to 1, 6, or 11, respectively. The yellow slurry was then transferred into the 20 mL Teflon-lined autoclaves, and kept at a filling ratio of 70% (volume fraction). Subsequently, the autoclave was heated to 180 °C in an oven. After crystallizing for 24 h, the resulting yellow products were filtered, washed with ethanol and distilled water several times, and dried at 100 °C for 10 h. For better presentation, we denoted the samples fabricated under various conditions as Bi_2WO_6-x (x = 1–8), as described in Table 1.

2.2. Characterization of Bi_2WO_6 photocatalysts

The crystal structures of the samples were characterized by X-ray diffraction (XRD) on a Rigaku D/max 2500 X-ray diffractometer (Cu K_α radiation, λ = 0.154, 18 nm), employing a scanning rate of 4.00° min^{-1}, in the 2θ range from 25° to 70°. A field emission scanning electron microscopy (FESEM, Japan JEOL, JSM-6700F) was employed to observe the surface morphologies of the resulting samples. The specific surface areas of Bi_2WO_6 samples were measured through nitrogen adsorption BET method (BET/BJH Surface Area, 3H-2000PS1). The Fourier transform infrared (FTIR) spectra were measured by FTIR spectrometer (America Perkin Elmer, Spectrum One). Raman spectra of Bi_2WO_6 samples were obtained by a micro laser Raman spectrometer (LabRam inva). Raman spectra were excited with the 514 nm line of an Ar^+ laser at an incident power of 20 mW. The diffuse reflectance spectra (DRS) were measured by a UV–vis spectrometer (UV-2550, Shimadzu). $BaSO_4$ was used as the reflectance standard material.

2.3. Photocatalytic activity studies

The photocatalytic activities of the as-prepared Bi_2WO_6 samples were evaluated using rhodamine B (Rh B) dye as a model compound. In experiments, the Rh B dye solution (0.01 mmol L^{-1}, 100 mL) containing 0.02 g of Bi_2WO_6 photocatalyst were mixed in a pyrex reaction glass. A 500 W Xe lamp (λ > 420 nm) was used to provide visible-light irradiation. A glass sheet was inserted between the lamp and the sample to filter out UV light (λ < 420 nm). Prior to illumination, the suspension was strongly magnetically stirred for 30 min in the dark for adsorption/desorption equilibrium. Then the solution was exposed to visible-light irradiation under magnetic stirring. At given time intervals, about 4 mL of the suspension was periodically withdrawn and analyzed after centrifugation. The Rh B concentration was analyzed by a UV-2550 spectrometer to record intensity of the maximum band at 552 nm in the UV–vis absorption spectra.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared Bi_2WO_6 samples prepared by hydrothermal procedure at different conditions. All diffraction peaks can be assigned to the orthorhombic Bi_2WO_6 (JCPDS no. 39-0256), which are consistent with the results reported by other researchers [6,12,30]. No peaks of impurities were detected from these patterns. The strong and sharp peaks indicate high crystallinity of the samples.

Raman spectra of the as-obtained Bi_2WO_6 samples are displayed in Fig. 2. It indicates several peaks in the range of 200–1000 cm^{-1}, which can be assigned to the stretches of the W—O bands [31,32]. In detail, the bands at 791 and 823 cm^{-1} are associated with antisymmetric and symmetric modes of terminal O—W—O, respectively. The band at 306 cm^{-1} can be assigned to translational modes involving simultaneous motions of Bi^{3+} and WO_6^{6-}. The intensity of the peak at 723 cm^{-1} is interpreted as an antisymmerric bridging mode associated with the tungstate chain. However, an obvious change of the Raman band intensity occurred in this range varying with the reaction conditions. The difference of the relative intensities of the antisymmetric and symmetric modes (791 and 823 cm^{-1}) of terminal O—W—O of the samples prepared under different conditions was observed, demonstrating that different space symmetries were formed and the variation or rearrangement of the

Table 1
Fabrication parameters and morphologies of the as-fabricated Bi_2WO_6 samples.

Sample code	Surfactant	Surfactant amount	Alkaline source	pH	Particle morphology
Bi_2WO_6-1	SDBS	0.03	$NH_3{\cdot}H_2O$	1	Rod-like
Bi_2WO_6-2	SDBS	0.03	$NH_3{\cdot}H_2O$	6	Flower-like
Bi_2WO_6-3	SDBS	0.03	$NH_3{\cdot}H_2O$	11	Disk-like
Bi_2WO_6-4	SDBS	0.06	$NH_3{\cdot}H_2O$	6	Flower-like
Bi_2WO_6-5	–	–	$NH_3{\cdot}H_2O$	1	Thread-like
Bi_2WO_6-6	–	–	$NH_3{\cdot}H_2O$	6	Spherical
Bi_2WO_6-7	–	–	$NH_3{\cdot}H_2O$	11	Spherical
Bi_2WO_6-8	SDBS	0.03	NaOH	6	Hollow spherical