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Nanosized $BiVO_4$ with high visible-light-induced photocatalytic activity: Ultrasonic-assisted synthesis and protective effect of surfactant

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ABSTRACT

Nanosized $BiVO_4$ with high visible-light-induced photocatalytic activity was successfully synthesized via ultrasonic-assisted method with polyethylene glycol (PEG). The $BiVO_4$ sample prepared under ultrasonic irradiation with 1 g PEG for 30 min was consisted of small nanoparticles with the size of *ca.* 60 nm. The effects of ultrasonic irradiation and surfactant were investigated. The nanosized $BiVO_4$ exhibited excellent visible-light-driven photocatalytic efficiency for degrading organic dye, which was increased to nearly 12 times than that of the products prepared by traditional solid-state reaction. Besides decoloring, the reduction of chemical oxygen demand (COD) concentration was also observed in the degradation of organic dye, further demonstrating the photocatalytic performance of $BiVO_4$. After five recycles, the catalyst did not exhibit any significant loss of photocatalytic activity, confirming the photocatalyst is essentially stable. Close investigation revealed that the crystal size, BET surface area, and appropriate band gap of the as-prepared $BiVO_4$ could improve the photocatalytic activities.

1. Introduction

Visible-light-driven photocatalytic technology can help to alleviate the problems of modern societies by splitting water for hydrogen production as green energy and degrading toxic pollutants [1–4]. Photocatalysts such as TiO_2 has been intensively investigated [5–8]. But it can only be excited by ultraviolet radiation that occupies about 4% of the solar light. Visible-light-driven photocatalysts have received considerable attentions because visible-light ($400\,nm < \lambda < 800\,nm$) occupies the main part of the solar spectrum. Therefore, the development of efficient visible-light-driven photocatalysts is becoming attractive and a great deal of effort has been devoted into this research [9].

Bismuth vanadate ($BiVO_4$) has been recognized as a visible-light-driven photocatalyst for water splitting and pollutant decomposing under visible-light irradiation [10–18]. Various methods have been used to synthesize $BiVO_4$ crystallites, such as aqueous process [10,19–22], hydrothermal process [23–25], organic decomposition method [26], chemical bath deposition [27], solution combustion synthesis method [28], flame spray pyrolysis [29], and solid-state reaction (SSR) method [30]. Recently, our group has reported a sonochemical route to synthesize $BiVO_4$ photocatalyst with relative high photocatalytic activity [31]. Currently, sonochemical processing is found to be facile and efficient for the preparation of various nanostructures at room temperature and atmosphere pressure [32–34].

It is well known that the photocatalytic activity closely relates with the diameter size and surface area etc. of the photocatalyst [35,36]. Thus, the synthesis of nanosized $BiVO_4$ photocatalysts with high surface area is a subject of considerable research interest to improve photocatalytic efficiency. Very recently, the ordered mesoporous monoclinic scheelite $BiVO_4$ was fabricated by nanocasting, using mesoporous silica KIT-6 as the replica parent template [37]. Compared to conventional $BiVO_4$, the product exhibited good photocatalytic performance in the photochemical degradation of methylene blue under visible-light irradiation. It was also confirmed that the nanosized photocatalyst could assuredly improve the photocatalytic activity.

Herein, the nanosized $BiVO_4$ with high visible-light-induced photocatalytic activity was prepared via the ultrasonic-assisted method with polyethylene glycol (PEG) as the surfactant. It was found that ultrasonic irradiation and protective effect of PEG played an important role in the formation of the photocatalyst and the final photocatalytic performance. The photodegradation of Rhodamine B (RhB) was employed to evaluate the photocatalytic activities of $BiVO_4$ under visible-light ($\lambda > 420\,nm$) illumination. Reduction of chemical oxygen demand (COD) concentration was observed in the degradation of RhB, further confirming the photocatalytic performance of $BiVO_4$. It is demonstrated that the nanosized $BiVO_4$ exhibits relatively high performance in the visible-light-driven photocatalysis.

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2. Experimental

2.1. Synthesis

All the reagents used in our experiments were of analytical purity and were used as received from Shanghai Chemical Company. In a typical preparation, aqueous solutions of $Bi(NO_3)_3{\cdot}5H_2O$ and NH_4VO_3 in 1:1 molar ratio were mixed together. Subsequently, polyethylene glycol 20000, as surfactant, was added into the above solution. The pH value of the final suspension was adjusted to about 7 by $NH_3{\cdot}H_2O$. Then the mixture was stirred for 1 h at room temperature. Afterward, the mixture was exposed to high-intensity ultrasonic irradiation (6 mm diameter Ti-horn, 600 W, 20 kHz) at room temperature in ambient air. The yellow precipitates were centrifuged, washed with de-ionized water and absolute ethanol, and then dried at 60 °C in air for 10 h. The obtained powders were then calcined at 450 °C for 2 h to produce crystalline products. All PEG series samples were ultrasonic irradiated with 0–2 g PEG for 30 min, while all ultrasonic irradiation series samples were prepared with 1 g PEG for different minutes.

For comparison, the sample which was ultrasonic irradiated for 30 min without PEG (P1), the sample prepared with 1 g PEG but no ultrasonic irradiation (U1), and the sample without PEG and ultrasonic pretreatment (BVO) were also prepared while other steps were the same as above. Bulk $BiVO_4$ was synthesized via traditional solid-state reaction according to Ref. [30], named as SSR-BVO.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the samples were measured on a D/MAX 2250 V diffractometer (Rigaku, Japan) using monochromatized Cu Kα ($\lambda = 0.15418$ nm) radiation under 40 kV and 100 mA and scanning over the range of $10^\circ \le 2\theta \le 70^\circ$. The crystal size was estimated from the Scherrer equation, $D = K\lambda/\mathrm{FWHM}\cos\theta$, where D is the crystal size, λ is the wavelength of the X-ray radiation and K usually is taken as 0.9, FWHM is the full width at half maximum in radian of the sample, and $2\theta = 28.6^\circ$. The morphologies and microstructures of as-prepared samples were analyzed by the scanning electron microscope (SEM) (JEOL JSM-6700F). UV–vis diffuse reflectance spectra of the samples were obtained on an UV–vis spectrophotometer (Hitachi U-3010) using $BaSO_4$ as the reference. Nitrogen adsorption–desorption measurements were conducted at 77.35 K on a Micromeritics Tristar 3000 analyzer after the samples were degassed at 200 °C for 6 h. The Brunauer–Emmett–Teller (BET) surface area was estimated using adsorption data. The photoluminescence (PL) spectra of the samples were recorded with a PerkinElmer LS55.

2.3. Photocatalytic test

Photocatalytic activities of the samples were evaluated by the photocatalytic decolorization of Rhodamine B under visible-light. A 500 W Xe lamp was used as the light source with a 420 nm cut-off filter to provide visible-light irradiation. In every experiment, 0.1 g of the photocatalyst was added into 100 mL RhB solution (10^{-5}–10^{-4} mol/L). Before illumination, the suspensions were magnetically stirred in the dark for 1 h to ensure the establishment of an adsorption–desorption equilibrium between the photocatalyst and RhB. Then the suspension was exposed to visible-light irradiation under magnetic stirring. At given time intervals, 3 mL suspension was sampled and centrifuged to remove the photocatalyst particles. Then, the UV–vis adsorption spectrum of the centrifugated solution was recorded using a Hitachi U-3010 UV–vis spectrophotometer. Chemical oxygen demand was estimated before and after the treatment using the $K_2Cr_2O_7$ oxidation method.

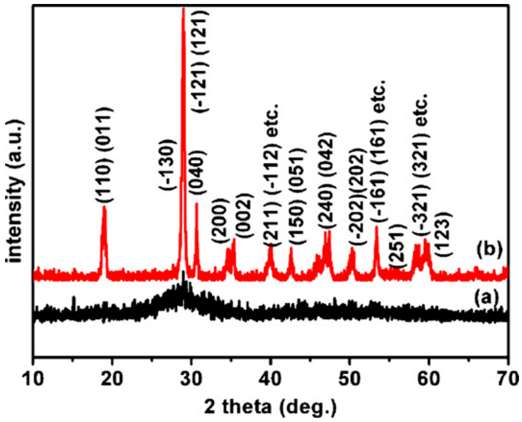

Fig. 1. XRD patterns of the calcined and uncalcined $BiVO_4$ samples: (a) uncalcined $BiVO_4$; (b) calcined $BiVO_4$.

Table 1
Size, band gap, BET surface area and degradation rate of $BiVO_4$ samples.

	Average size (nm)	BET (m^2/g)	Band gap (eV)	Degradation rate (%)
BVO	183	7.25	2.28	28
U1	645	9.09	2.24	42
P1	65	10.05	2.18	65
BVO-P-U	51	12.03	2.13	100

3. Results and discussion

3.1. Crystal structure

The phase and composition of the calcined sample, as well as the uncalcined sample were characterized by XRD, as shown in Fig. 1. The pattern of Fig. 1a indicates that the uncalcined $BiVO_4$ obtained after ultrasonic irradiation for 30 min with 1 g PEG is poorly crystallized. However, the calcination favors the formation of well-crystallized $BiVO_4$ comparatively, and the diffraction peaks of this sample (named as BVO-P-U) agree well with those of the pure monoclinic $BiVO_4$ according to the JCPDS No. 14-0688, as revealed in Fig. 1b. The cell constants calculated by the least squares refinement method are as follows: (a) 5.192 Å, (b) 11.701 Å, and (c) 5.091 Å, which are in agreement with the reported values (JCPDS No. 14-0688) [20,37]. The average crystallite size calculated from the strongest diffraction peak using the Scherrer equation is about 51 nm [37,38]. The average size of the other samples which were also calculated from the XRD (not given) were shown in Table 1.

3.2. Morphology and microstructure

The morphology and microstructure of the $BiVO_4$ samples were revealed by scanning electron microscopy (SEM). Fig. 2A is the SEM image of the BVO-P-U sample, showing that it is composed of well-separated nanoparticles with an average size of about 60 nm. The crystalline size is in good agreement with the value evaluated using Scherrer equation based on XRD patterns. To investigate the effect of ultrasonic irradiation and PEG on the morphology of $BiVO_4$ products, the SEM of P1, U1, and BVO samples were also shown in Fig. 2B, C, and D, respectively. As shown in Fig. 2B, most of the P1 particles which was ultrasonic irradiated for 30 min without PEG connected with each other and fusion was induced in the absence of PEG while the BVO-P-U were well dispersed. The morphology of U1 sample which was prepared with 1 g PEG but no ultrasonic irradiation was shown in Fig. 2C. The U1 sample is composed of rod-like particles with the average size of about 1000 nm. The morphology of the BVO sample without ultrasonic irradiation and PEG was revealed to be