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Influence of Heat Treatment on Photocatalytic Performance of BiVO_4 Synthesized by Hydrothermal Method

DOI 10.1515/hmp-2015-0070

Received March 20, 2015; accepted September 19, 2015

Abstract: Monoclinic BiVO_4 photocatalyst was successfully synthesized by hydrothermal method under appropriate temperature. The photocatalytic performance of BiVO_4 was improved by calcining at appropriate temperature. The structural and morphological properties of the synthesized BiVO_4 photocatalysts were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. It is confirmed that the photocatalytic activity of the prepared catalysts was evaluated by the photodegradation of RhB under visible-light irradiation. BiVO_4 calcined under appropriate temperature exhibited higher photocatalytic activity than uncalcined BiVO_4 under visible light irradiation because calcination might effectively increase the purity of monoclinic bismuth vanadate.

Keywords: BiVO_4 , hydrothermal method, calcinations, photocatalytic activity

Introduction

BiVO_4 as an attractive visible light catalyst has received considerable interest in recent years because it is non-toxic, stable and high-response to visible light.

Actually, BiVO_4 has been widely used in previous investigations [1–5], especially in the visible light photocatalytic degradation. Since the excellent property of monoclinic BiVO_4 was discovered, many methods for preparing inorganic materials are used in the preparation of BiVO_4 [6, 7].

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As a novel photocatalytic semiconductor material, BiVO_4 has a broad application prospects. So it is meaningful to improve photocatalytic activity of BiVO_4 . Many methods are used for improving photocatalytic activity of BiVO_4 [8–14]. Influence of calcination on photocatalytic performance of BiVO_4 has been rarely reported.

In the present study, the photocatalytic activities of as-prepared BiVO_4 samples were evaluated by the degradation of RhB under visible-light irradiation and the advantage of calcination has also been discussed.

Experimental details

Synthesis of BiVO_4 photocatalysts

A series of monoclinic BiVO_4 samples were synthesized using the hydro-thermal method with appropriate temperature and holding time. A typical preparation process was described below. 0.01 mol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was firstly dissolved in 40 mL of 3.6 mol/L HNO_3 to form a homogeneous solution A. Secondly, 0.01 mol of EDTA-2Na was dissolved in 40 mL distilled water to form a homogeneous solution B. And NH_4VO_3 was dissolved in 70°C distilled water with mechanical agitation until the dissolution was complete to form a homogeneous solution C, and then followed by the addition of B with mechanical agitation until the dissolution was complete to form a homogeneous solution D. At length, the solution D was added into A to form a resulting suspension.

Then, the resulting suspension was transferred into a Teflon recipient inside of stainless steel autoclave. The hydrothermal treatment was under appropriate temperature and holding time. The precipitate was obtained after cooled down to room temperature. The precipitate was then filtered, repeatedly washed with absolute ethyl alcohol and distilled water three times and dried overnight at 60°C to get the initial samples. Then, the initial samples were submitted to a further calcination under different temperatures and holding time in a muffle furnace. The samples were obtained after cooled down to room temperature in the furnace.

Characterization and photocatalytic activity

X-ray diffraction (XRD) patterns were recorded by X-ray diffractometry (Rigaku D/Max-2500) with Cu K α radiation ($\lambda = 0.15406$ nm) and the range of diffraction angles was scanned from 10° to 70°. Scanning electron microscopy (SEM) observations.

The photocatalytic activities of BiVO₄ catalysts for RhB decolorization were evaluated under visible-light irradiation using a 500 W Xe lamp as the light source. Experiments were conducted at ambient temperature and procedures were as follows: an aqueous suspension of RhB (50 mL, 5 mg/L) was placed in a quartz tube, and then 100 mg photocatalysts were added. Before illumination, the suspensions were mechanically stirred in the dark for 30 min to ensure the adsorption-desorption equilibrium between the catalysts and the dye. Then 5 mL aliquots were withdrawn and centrifuged to remove the photocatalyst powders for analysis every 30 min. The concentration of remnant dye was subsequently determined by UV-vis spectroscopy at the wavelength of 552 nm during the photodecolorization process.

Results and discussions

Figure 1 shows the XRD patterns of the as-prepared samples calcined under different temperatures for 1 h. Figure 1 shows that the principal crystalline phases under different calcination temperatures are all monoclinic phase. For BiVO₄ without calcination, the pattern shows that the powders crystallized as a mixture of Bi₄V₂O₁₁ (PDF card 44-0358) and monoclinic BiVO₄ (PDF card 14-0688). For BiVO₄ calcined at 300°C, the pattern shows that the powders crystallized as a mixture of Bi₄V₂O₁₁ and

monoclinic BiVO₄. And the consist of Bi₄V₂O₁₁ has increased slightly. As the temperature increases to 400°C and 500°C, the peaks indicate that Bi₄V₂O₁₁ gradually vanishes and all diffraction peaks can be assigned to the pure monoclinic structure. For the samples calcined at 600°C, some BiVO₄ gradually transforms into Bi₄V₂O₁₁. The results suggest that the temperature of calcination is an important factor in preparing pure monoclinic BiVO₄.

Figure 2 shows SEM images of surfaces of BiVO₄ prepared with different heat treatment temperatures at 300°C, 400°C, 500°C and 600°C. It reveals that the distribution of grain is uniform, the grain size is small, and the agglomeration phenomenon is slightly at 300°C and 400°C. When the temperature rises to 500°C, the grain size gradually becomes larger, and the grain has a uneven distribution. Figure 2(c) shows that the annex phenomenon happens and there is too big or too small grain. Figure 2(d) shows that the grains become larger, which may be due to the high temperature providing the enough energy. Thus, the generated smaller grain gradually began to melt and reformed to larger crystal particles. This phenomenon is known as “big eat small” in the field of materials. SEM pictures verify the XRD patterns that peak intensity decreased at 500°C and 600°C, this is because the agglomeration of grains.

Figure 3 shows the degradation rate of RhB of samples at different calcination temperatures for 1 h. As can be seen from the chart, the degradation effect of RhB solution of 400°C is the highest and is higher than the samples without calcinations. The samples calcined at other temperature are lower than the samples without calcinations. This is because that with the calcination temperature continuing to rise, the samples become agglomeration. Combined with the SEM image analysis, the grain size is the minimum and has a uniform distribution at 400°C. The small grain size makes charge carrier mobility relatively short and photogenerated electron and hole compound difficult, so better catalytic activity in the degradation process is presented.

Figure 4 shows the XRD patterns of the as-prepared samples calcined at 400°C for different time. Figure 4 shows that the principal crystalline phases under different hydrothermal treatment temperatures are all monoclinic phase. For BiVO₄ without calcination, the pattern shows that the powders crystallized as a mixture of tetragonal Bi₄V₂O₁₁ (PDF card 44-0358) and monoclinic BiVO₄ (PDF card 14-0688). For BiVO₄ as-calcined for 0.5 h, the pattern shows that Bi₄V₂O₁₁ gradually transforms into monoclinic BiVO₄. As the time increases, the peaks indicate that all diffraction peaks can be assigned to the pure monoclinic structure. But for BiVO₄ as-calcined for 5 h, BiVO₄

Figure 1: XRD patterns of BiVO₄ with different heat treatment temperatures for 1 h.

Figure 2: SEM pictures of BiVO_4 with different heat treatment temperatures (a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C.

Figure 3: Degradation charts of BiVO_4 samples with different heat treatment temperatures.

Figure 4: XRD patterns of BiVO_4 with different heat treatment time at 400°C.

gradually transforms into Bi_2O_3 (PDF card 45–1344). The diffraction peak of 3 h is the sharpest strongest, which means the degree of crystallinity is the best of 3 h. The results suggest that calcination can improve the degree of crystallinity, and the time of calcination is an important factor in preparing pure monoclinic BiVO_4 .

Figure 5 shows SEM images of surfaces of BiVO_4 prepared at 400°C for 0.5 h, 1 h, 3 h and 5 h. It reveals that with the prolongation of time, the grain size gradually becomes more uniform but too long holding time lead to the agglomeration of grains, and the grain size becomes abnormally large. Figure 5(a) shows the samples with a holding time of 0.5 h. The grains have a good dispersion, but the grain size is large and uneven. Figure 5(b) shows

the samples with a holding time of 1 h. The grain size is small and the distribution is uniform. Figure 5(c) shows the samples with a holding time of 3 h. It reveals that small particles connect together, forming a homogeneous spherical. When the holding time is 5 h, the particles grow into larger size, reaching 1–2 μm . It is because the ion electronegativity, not the dispersion of the system.

Figure 6 shows the degradation rate of RhB solution of samples at 400°C for different time. Figure 6 reveals that the degradation rate of the sample of 3 h is the highest. And the samples of 3 h and 1 h are the higher than the sample without calcination. This may be because the stronger diffraction peak of 3 h on XRD pattern and the degradation is mainly decided by the

Figure 5: SEM pictures of BiVO₄ samples with different heat treatment time (a) 0.5 h, (b) 1 h, (c) 3 h, (d) 5 h.

Figure 6: Degradation charts of BiVO₄ samples with different heat treatment time.

hydroxyl radical on its surface. The degradation rate of samples of 3 h and 1 h reaches higher. It is because the grain size increases and the increasing of the grain size lead to smaller specific surface area compared with the samples without calcination, the degradation rate of sample under calcination is improving.

Conclusions

Monoclinic BiVO₄ photocatalyst was successfully synthesized by the hydrothermal method under appropriate temperature. Heat treatment is an important factor in

preparing pure monoclinic BiVO₄ photocatalytic materials. Temperature and time of heat treatment have a considerable influence on the photocatalytic activities of the as-synthesized BiVO₄. The sample with a heat treatment temperature of 400°C for 3 h has the best photocatalytic activities.

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