

Effects of pH on the Morphology and Photocatalytic Performance of BiVO₄ Prepared via Hydrothermal Method

Xingxing Gao¹, Jian Wang², Hongbo Xu^{1,a} and Jianglong Yu^{1,3}

¹School of Chemical Engineering, University of Science and Technology Liaoning, High-Tech District 185 Qianshan Middle Road, Anshan 114051, China.

²School of Mining Engineering, University of Science and Technology Liaoning, High-Tech District 185 Qianshan Middle Road, Anshan 114051, China.

³Chemical Engineering, University of Newcastle, Callaghan NSW 2308, Australia

^ainkdxhb@163.com

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Abstract. BiVO₄ with different morphologies were synthesized via a controllable dodecylamine-assisted hydrothermal method. The effect of pH on the crystallinity, morphology and optical absorption property of BiVO₄ was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-vis Diffuse Reflectance Spectra techniques (UV-vis DRS). The photocatalytic efficiencies were evaluated by the degradation of (MB) under visible-light irradiation. It is worthy to note that the obtained monoclinic scheelite BiVO₄ (*m*-BiVO₄) prepared at pH 1 possessed a spherical microstructure, low band gap energy, and exhibited the highest photocatalytic activity of the samples, decolorizing up to 98.2 % of MB upon visible light irradiation for 4h. The reason for the different photocatalytic efficiencies of the BiVO₄ samples obtained at different pH was investigated by considering the structure and morphology.

Introduction

Semiconductor photocatalysis has attracted extensive attention as a potential solution to worldwide energy shortage and for alleviating environmental degradation [1, 2]. Monoclinic bismuth vanadate (*m*-BiVO₄), with a narrow band gap (2.4 eV), has been extensively investigated as an attractive advanced material for the photocatalytic degradation of organic pollutants [3, 4] and water splitting under visible light irradiation [5]. The photocatalytic performance of *m*-BiVO₄ is strongly dependent on its morphology and microstructures like other photocatalysts. Hydrothermal synthesis is widely used because the microstructures can be controlled by tuning the experimental parameters such as precursor concentration, the pH value, the nature of the surfactant, the temperature and the reaction medium. It is found that the pH values of the precursor solution have the great effects on the phase and morphology of BiVO₄ powders [6-8]. Therefore, it is meaningful to develop a simple, one-step hydrothermal route to synthesize *m*-BiVO₄ with various sizes and shapes by the mediation pH values.

In this work, uniform *m*-BiVO₄ crystals with different morphologies have been synthesized in high yield by an improved hydrothermal approach through tuning the pH value of a mixed solvent composed of water and ethylene glycol. The influence of pH value on the controllable morphology of *m*-BiVO₄ was studied. The effect of different morphologies BiVO₄ on photocatalytic property was also investigated through the degradation of methylene blue (MB) under visible-light irradiation ($\lambda > 400$ nm).

Experimental Section

Synthesis. In a typical preparation, 4 mmol Bi(NO₃)₃·5H₂O, 4 mmol of NaVO₃ and 12 mmol Dodecylamine was added into 40 mL of mixed solvents (ultrapure water and ethylene glycol with a volume ratio of 1:1). The pH of the reaction solutions were adjusted by HNO₃ solutions. After being stirred vigorously, the solution was transferred into a Teflon-lined stainless steel autoclave with 50 mL capability and heated at 120 °C for 12 h.

Characterization. The as-synthesized samples were examined by X-ray diffractometry (XRD) measurement on a Rigaku-DMax 2400 diffractometer equipped with graphite monochromatized $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$). The morphology of the samples was investigated by using a scanning electron microscope (SEM, Hitachi S-3500N). The surface area was determined with the Brunauer–Emmett–Teller (BET) method (TriStar II3020, Micromeritics). The UV-Vis absorption spectra were recorded on a UV-vis spectrophotometer (Shimadzu, Model UV-2550) in the wavelength range of 200–800 nm.

Photocatalytic experiments. Photocatalytic activities of samples were determined by the degradation of methylene blue (MB) aqueous solution under visible light ($\lambda > 400 \text{ nm}$). Experiments were performed at ambient temperature as follows: 0.025 g of photocatalyst was added to 50 mL MB (10 mg/L) aqueous solution. The mixture was first sonicated for 5 min and then kept in the At the same irradiation time intervals, analytical samples were taken from the suspension. The concentration analysis of MB was determined by using a Hitachi U-3010 spectrophotometer.

Results and discussion

In solution, the pH value plays an important role in the formation of the crystal structure. It is observed that the XRD patterns of all of the samples obtained at pH = 1, 3, 5, 7, 9 matched well with that of the monoclinic BiVO_4 samples (JCPDS Card No. 14-0688), and no other impurity peaks as shown in Fig1 (A).

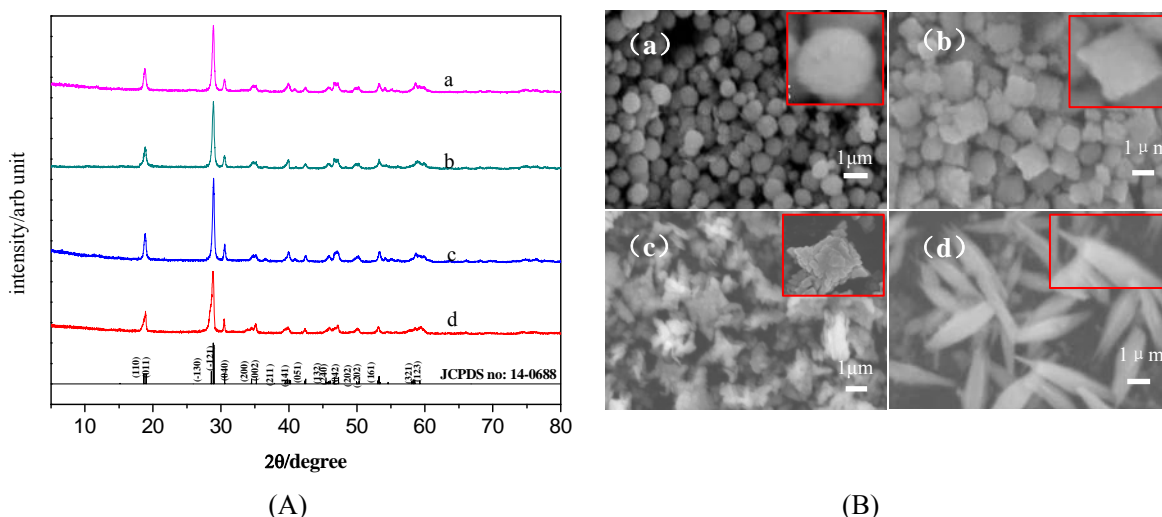


Fig.1 (A) XRD patterns and (B) SEM images of the as-prepared BiVO_4 samples obtained at different pH values. pH: (a) 1, (b)4, (c)7, (d) 9.

SEM was used to observe the morphologies of BiVO_4 samples. Fig.1 (B) was the SEM images of the BiVO_4 products obtained at different pH value. When the pH is adjusted to be 1, the SEM images show the product consists of submicron spheres with diameters ranging from 600 to 800 nm. As the pH reaches to 4, the as-synthesized products are almost square-like BiVO_4 samples with a length of 1 μm, approximately. It can be seen that octopod-like BiVO_4 with the pH value increase continuing (pH = 7). It can be observed that diamond-like BiVO_4 , which the long diameter and short diameter were 4.78 μm and 0.78 μm, respectively.

Fig.2 (A) was the UV-Vis DRS of BiVO_4 samples, they showed strong absorption in both UV-and visible-light regions. We used E_g to evaluate the optical performance of BiVO_4 samples. Their band gaps could be estimated based on the formula $(\alpha h\nu)^2 = A(h\nu - E_g)^n$, where α , $h\nu$, A , E_g , n were absorption coefficient, incident photon energy, constant, the band-gap energy and an integer, respectively. Among them, n depends on the characteristics of the optical transition in a

semiconductor. BiVO₄ pertain to direct transition, so $n=1$. We can estimate the band-gap energy (E_g value) of BiVO₄ from a plot of $(ah\nu)^2$ versus the photon energy ($h\nu$), as shown in the insert of Fig.2(A). The intercept of the tangent to the x axis will fit well with the band-gap energy (E_g value). The estimated band-gap energies of the as-obtained BiVO₄ fell into the range of 2.27-2.38 eV. Compared with other morphologies, BiVO₄ microspheres possessed a much lower band gap energy (2.27 eV). This result indicated that BiVO₄ microspheres may show better photocatalytic activity for the degradation of organic dyes under visible-light irradiation.

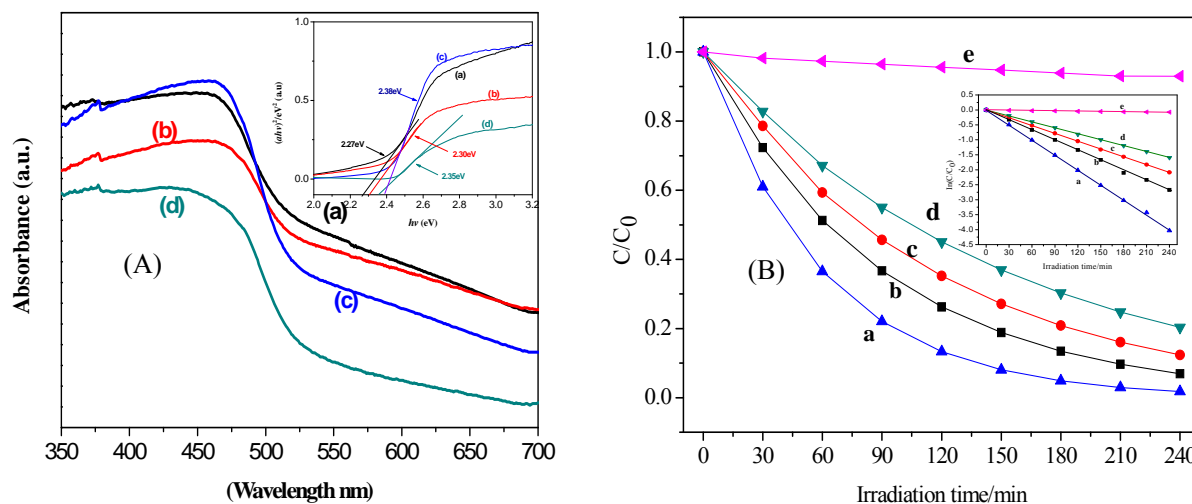


Fig.2(A) UV-Vis DRS of samples (The insert is the plots of $(ah\nu)^2$ versus $h\nu$ of BiVO₄ samples) (B) Photodegradation efficiencies of MB as a function of irradiation time for different photocatalysts. (The insert is the dynamics of MB degradation reaction.) (a) spherical BiVO₄, (b) square-like BiVO₄, (c) octopod-like BiVO₄, (d) diamond-like BiVO₄, (e) without catalyst.

In order to evaluate the photocatalytic activities of the as-synthesized BiVO₄ samples, the degradation ability of MB dye under visible-light irradiation was studied, as shown in Fig.2 (B). We conducted the experiments of MB direct photolysis (blank experiment) under identical conditions. From the catalytic studies, only 8 % MB could be photolyzed under visible-light irradiation within 4h. The catalytic activity order of the different photocatalysts was as follows: spherical BiVO₄ > square-like BiVO₄ > octopod-like BiVO₄ > diamond-like BiVO₄. Among the four BiVO₄ samples, spherical BiVO₄ exhibited the best visible-light-driven photocatalytic activities: the degradation rate of MB increases to 98.2 % after 4h irradiation, much higher than that of square-like BiVO₄ (ca. 93.1%), octopod-like BiVO₄ (ca. 87.6%) and diamond-like BiVO₄ (ca. 79.7%). According to the plots in the insert of Fig.2 (B), the degradation of MB follows the pseudo-first-order kinetic formula. The average value of apparent rate constant for spherical BiVO₄ ($k=0.0167 \text{ min}^{-1}$) was 2.5 times higher than the diamond-like BiVO₄ ($k=0.0067$). It is well-known that the activities of photocatalysts depend on the specific surface area, crystallite size, crystal structure, morphology[9]. The BET results showed that the specific surface area of BiVO₄ microspheres was 15.8 m²/g, the square-like BiVO₄ was 10.6 m²/g, the octopod-like BiVO₄ was 8.1 m²/g and the diamond-like BiVO₄ was 7.3 m²/g. The larger the surface area of the materials, the higher the photocatalytic activity they may exhibit. Because higher specific surface area means more active sites on catalyst surface at the same catalyst loading. The enhanced photocatalytic activity of spherical BiVO₄ can be attributed to the novel spherical structure and the specific surface areas, which could provide more active sites for the degradation of MB. Base on the above characterization results and activity data, we concluded that the photocatalytic performances of these BiVO₄ samples were greatly different and strongly dependent on the morphology and the specific surface area.

Conclusions

We have successfully prepared BiVO₄ photocatalysts with different morphologies via a facile, pH-controlled hydrothermal route. It is shown that the pH value played an important role in the formation of different microstructures. The band-gap energy, specific surface area and special morphology (spherical structure at pH 1) result in the excellent photocatalytic activities of the *m*-BiVO₄ to degrade MB under visible-light irradiation.

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