

Preparation and Activities of Visible-Light-Driven BiVO₄ by Doping Zn²⁺ via Solid State Method

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Abstract—Using Bi(NO₃)₃·5H₂O, NH₄VO₃ and Zn(NO₃)₂·6H₂O as raw material, Zn-doped BiVO₄ photocatalysts were successfully prepared by a low-temperature grinding synthesis. And the samples were characterized by X-ray diffraction (XRD), Infrared spectroscopy (FT-IR) and UV-Vis diffuse reflectance spectroscopy (DRS). The Methyl Orange (MO) was simulated as the sewage under the visible light to study the influence of the illumination time and the amount of photocatalyst. The visible-light absorption scope of BiVO₄ was broadened by doping Zn²⁺, the UV-Visible absorption edge was slightly red shifted and the band gap was narrowed comparing with the pure BiVO₄. It was found that the catalytic effect of the Zn-doped catalysts was enhanced under the visible-light irradiation. The cause of enhanced catalytic effect has also been analyzed and discussed in the article.

Keywords- BiVO₄; Zn-doped; photocatalysis; solid state method; visible light

I. INTRODUCTION

In recent decades, various researches have focused on the photocatalysis, and TiO₂ has attracted considerable interest for its well photocatalytic property [1-2]. Undoubtedly, it has become one of the most vital photocatalyst. However, with its wide band gap energy of 3.2eV [3], the application of the wide-band gap materials is limited in UV light region. BiVO₄ has been regarded as a kind of novel and environmental semiconductor photocatalysis, and it also brings a widespread prospect to water decomposition and organics photocatalytic degradation because of its narrow band gap, no toxicity and good stability [3]. The photocatalytic property of BiVO₄ is strongly dependent on its structure. Generally, BiVO₄ is found to mainly exist in three crystalline phase including zircon-tetragonal type (z-t), scheelite-tetragonal type (s-t) and scheelite-monoclinic type (s-m)[4]. And the scheelite-monoclinic structure possesses higher photocatalytic activity compared with tetragonal phase. Meanwhile, the synthetic method of BiVO₄ is important for its structure and property. Several synthetic routes have previously been employed to prepare BiVO₄ sample

such as sonochemical route [5], hydrothermal method [6], impregnation method[7], aqueous phase precipitation[8], and sol-gel method[9], ect.

However, the activity of pure BiVO₄ needs to be improved due to its poor adsorptive performance and easy recombination of photo-induced carriers [4, 6, 7]. We can load BiVO₄ with some metals to improve its absorption and obtain photocatalyst with enhanced catalytic activity. Up to now, there are many reports on development of doping BiVO₄ with Pd [7], Cu [10], Ag [11], Pt [12] mainly by means of hydrothermal method or precipitation procedure, however there is nothing about BiVO₄ doped by Zn on photocatalyst except on environmentally friendly yellow pigments[13]. And precursor Zn(NO₃)₂ was used for spot array preparation in aqueous solution, it show that doping of Zn into BiVO₄ increases the photocurrent for sulfite oxidation on BiVO₄ for scanning electrochemical microscopy (SECM) [14]. In this work, we based on other reports to creatively research the preparation and Photocatalytic activity of Zn-doped BiVO₄. Using Bi(NO₃)₃·5H₂O, NH₄VO₃ and Zn(NO₃)₂·6H₂O as raw material, controlling the amount of Zn(NO₃)₂·6H₂O, the scheelite-monoclinic BiVO₄ were successfully prepared by grinding for a certain time. Also, it could be obtained by low-temperature grinding synthesis. Simultaneously, we studied the effect of reaction time, grinding time and the amount of Zn²⁺ on the formation and crystal structure of Zn-doped BiVO₄. The visible-light photocatalytic properties of the as-prepared samples were evaluated by the photocatalytic degradation of methyl orange (MO), as well as the catalytic efficient were researched by altering the illumination time and the amount of photocatalyst.

II. EXPERIMENTAL

A. Synthesis of Zn-doped BiVO₄ samples

In this work, the synthesis of Zn-doped BiVO₄ was shown in the following way: 5.0 mmol (2.45 g) Bi(NO₃)₃·5H₂O, 5.0 mmol (0.58 g) NH₄VO₃ and Zn(NO₃)₂·6H₂O were uniformly mixed and fully grinded in agate mortar, then stopped grinding until mixture

turned to be reddish brown slurry. After that, mixed solution was transferred to a ceramic crucible, and dried in an oven at 120 °C for 12 h. Next, dried powder was taken from ceramic crucible and washed with distilled water and anhydrous alcohol for three times, respectively. After centrifugation, the as-obtained substance was dried in vacuum environment at 60°C for 4h then Zn-doped BiVO₄ samples were prepared. Blank experiment was also carried out to well compare the superiority of product, in which mixing and grinding the same amount of Bi(NO₃)₃·5H₂O and NH₄VO₃ until white powder entirely transformed into orange liquid and dried it at 120°C for 12h to remove its absorbed moisture and crystal water formed during reactions, finally the pure BiVO₄ samples were obtained. The chemical reagents mentioned above were analytical grade and were purchased from Aladdin Chemical Co.

B. Characterization

The X-ray diffraction (XRD) patterns of samples were obtained on X-D6 X-ray diffractometer with Cu K α radiation ($\lambda=0.15406$ nm) in the range of $2\theta=10-80^\circ$ and the tube voltage and the applied current were 40kV and 40mA, respectively. A UV-Vis spectrophotometer (5A2PO54001) was used to obtain the absorption spectra of samples, which worked at a scan rate of 4500 nm/min and sample every two minutes. Infrared spectroscopy analysis was performed on Fourier transform infrared spectroscopy (NICOLET5700x, Thermo Electron).

C. Photocatalytic activity of Zn-doped BiVO₄ samples

0.01 g Zn-doped BiVO₄ catalysts was added into 10 mL methyl orange solution (10 mg/L) simulated as the sewage, in which photocatalyst powder was uniformly dispersed by ultrasonic probe for 1-2 min, so as to prevent them agglomerating. After being preheated 30 min, the system was irradiated under visible light and the reaction time was tunable. After that, the solution was transferred into centrifuge tube and centrifuged (3000 rpm, 30 min) to obtain the supernatant. Then, the concentration of methyl orange was analyzed by measuring the absorbance at 465 nm wavelength, and the degradation rate was calculated by the Lambert-Beer law.

III. RESULTS AND DISCUSSION

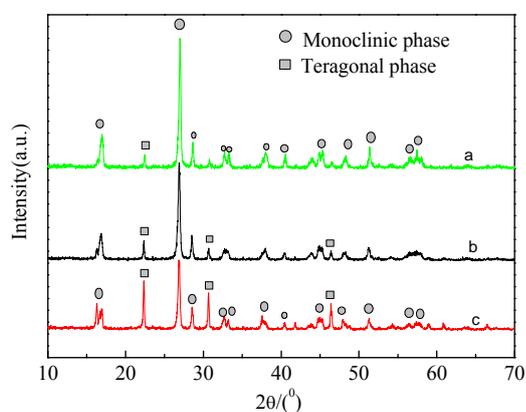


Figure 1. XRD patterns of Zn-doped BiVO₄ at different grinding time; a: 20 min; b: 15 min; c: 5 min

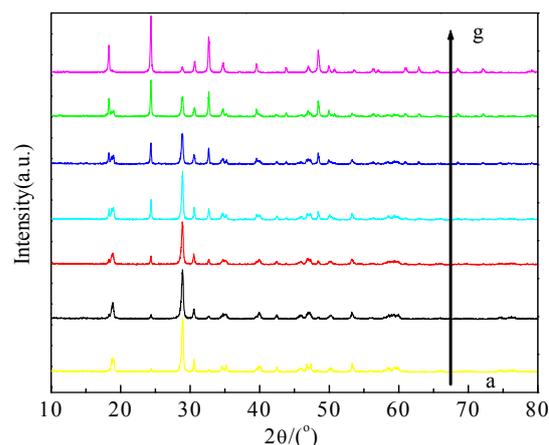


Figure 2. XRD patterns of Zn-doped BiVO₄ with different drying time at 120°C; a: 8 h; b: 7 h; c: 6 h; d: 5 h; e: 4 h; f: 3 h; g: 2 h.

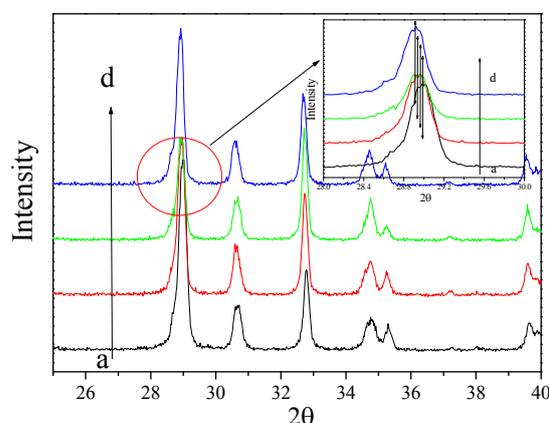


Figure 3. XRD patterns of Zn-doped BiVO₄ with different Zn content; a: pure BiVO₄; b: 10 mg Zn(NO₃)₂; c: 15 mg Zn(NO₃)₂; d: 20 mg Zn(NO₃)₂

A. The influence of grinding time and drying time.

In the experimental section, Zn-doped BiVO₄ catalysts were successfully prepared by a low-temperature grinding synthesis. Fig1 shows XRD patterns of Zn-doped BiVO₄ at different grinding time. Although all samples displayed two kind of characteristic patterns for monoclinic and tetragonal phase, tetragonal phase gradually became weaker and weaker with the increase of grinding time. It has been reported that the monoclinic structure shows better photocatalytic performance, so these samples were dried at 120 °C for enhancing phase transformation. The Figure 2 illustrates the XRD diffraction patterns of novel photocatalysts with different drying time, which show samples basically converted to monoclinic BiVO₄ when dried for 8 h(Fig.1,a). However, the characteristic peaks of Zn weren't clearly observed in all diffraction patterns and we infer that the formed weak peak may be caused by the full dispersion and the small amount of Zn content.

B. The influence of Zn²⁺ content

The XRD patterns of samples with different Zn content are as shown in Fig.3. The main peak and the second strongest peak at $2\theta=28.822^\circ$ and 28.947° corresponding to the (-121) and (121) planes of monoclinic BiVO₄, and

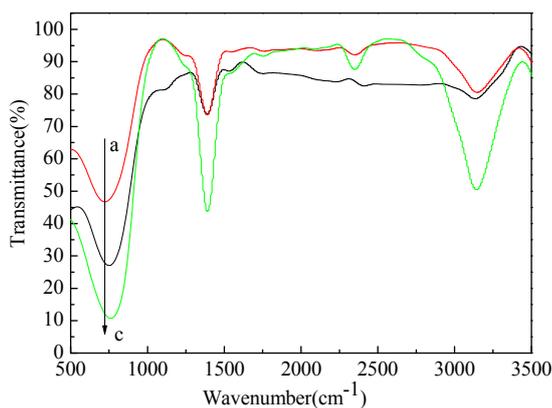


Figure 4. Infrared spectra of Zn-doped BiVO₄ with different Zn content; a: 10 mg Zn(NO₃)₂; b: pure BiVO₄; c: 20 mg Zn(NO₃)₂.

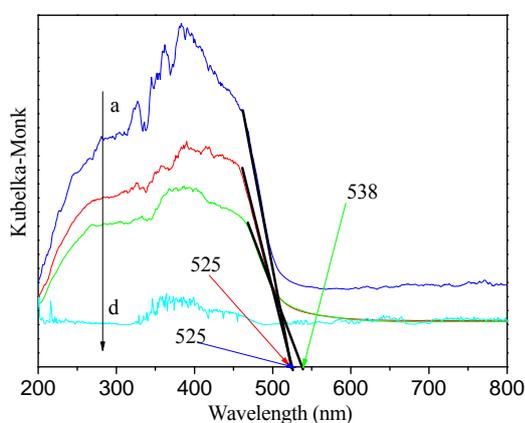


Figure 5. UV-vis diffuse reflectance spectra of pure and Zn-doped BiVO₄ samples; a: 25 mg Zn(NO₃)₂; b: 10 mg Zn(NO₃)₂; c: 15 mg Zn(NO₃)₂; d: pure BiVO₄.

respectively, which match well with the standard card (JCPDS83-1700). And these angles all slightly become smaller with the increase of the Zn content. We can know the lattice spacing is widen from Bragg equation and indirectly demonstrate the formation of lattice distortion by doping Zn, which is also confirmed by following way such as SEM.

C. FT-IR study

Although the existence of Zn species has been indicated in XRD analysis, their specific places need to be further studied by XPS. According to Pauling rule, it's necessary for Zn²⁺ to be enclosed by oxygen anion. The characteristic peak at 505 cm⁻¹ may correspond to Zn-O bond (Fig. 4a, c) and no peak is observed in Fig. 4b, which is consistent with the literature.

D. DRS study

UV-vis diffuse reflectance spectra of pure and Zn-doped BiVO₄ series samples are depicted in Fig. 5. It can be seen that the Zn²⁺ content has significant effect on absorption, and Zn-BiVO₄ composite has apparent absorption edge and range comparing to pure BiVO₄, especially in the visible light region more than 400 nm. The threshold wavelength of Zn-doped BiVO₄ with 25 mg,

10 mg and 15 mg Zn(NO₃)₂ are corresponding to 525 nm, 525 nm and 538 nm, while the value of band gap energy are 2.36 eV, 2.36 eV and 2.30 eV, respectively, which were calculated by $E_g = 1240/\lambda_g$ and relative smaller than the reported values. It shows that the band gap of doped samples increased (i.e. red shift) at first and then increase (i.e. blue shift) with the increase of Zn content.

E. Photoactalytic activity

Fig. 6 shows the effect of Zn content and the amount of sample on the photodegradation activity of methyl orange under the visible light irradiation, it is easy to find that the amount of photocatalysts is a vital factor, and in general, the degradation rate would fall with the increase of the amount of photocatalysts. Meanwhile, it is worth noticing that the concentration of methyl orange apparently will decrease when increase the Zn content, and the differences between the photocatalysts are even enlarged. Take 5 g samples for example, the remaining concentration of methyl orange in the presence of pure BiVO₄ is 1.25-fold greater than that in the existence of Zn-doped BiVO₄ doped with 25 mg Zn(NO₃)₂.

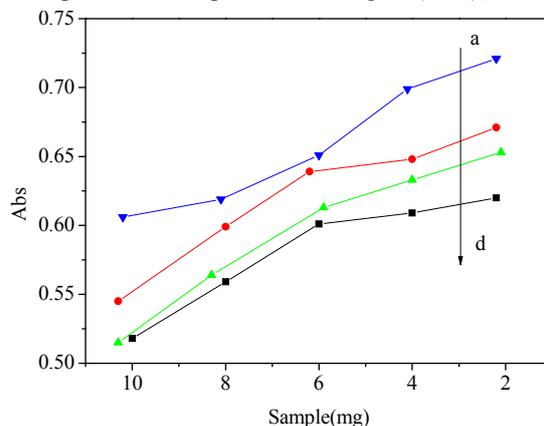


Figure 6. The absorption of pure and Zn-doped BiVO₄ series samples; a: pure BiVO₄; b: 10 mg Zn(NO₃)₂; c: 15 mg Zn(NO₃)₂; d: 25 mg Zn(NO₃)₂.

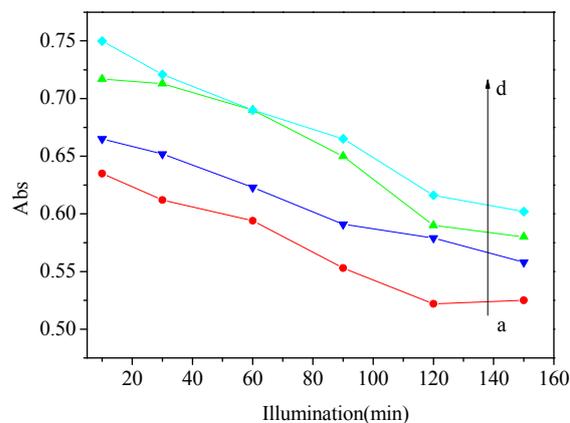


Figure 7. the effect of different Zn-doped BiVO₄ samples and illumination time (a: pure BiVO₄; b: 15 mg Zn(NO₃)₂; c: 20 mg Zn(NO₃)₂; d: 25 mg Zn(NO₃)₂).

The experimental results of MO degradation with Zn-doped BiVO₄ catalysts at different Cu content and illumination time are shown in Fig.7. Under a certain range of illumination time, the absorption of MO has been declined and the decrease is distinct as the illumination time increase, which illustrate that the degradation rate has been increased. However, the absorption arrive at a specific value or the decrease rate become small when the reaction time is over 120min, so the excess time could be detrimental to the photocatalytic degradation efficiency. And for these samples with the same amount, the more Zn content is, the biggest efficiency could be obtained. While the efficiency of Zn-doped BiVO₄ doped with 25 mg Zn(NO₃)₂ in 60 min is equal to that of Zn-doped BiVO₄ doped with 10 mg Zn(NO₃)₂ in 12min.

IV. CONCLUSIONS

In this work, using Bi (NO₃)₃·5H₂O, NH₄VO₃ and Zn(NO₃)₂·6H₂O as raw material, and Zn-doped BiVO₄ photocatalysts were successfully prepared by a low-temperature grinding synthesis. Monoclinic structure could be obtained by controlling the grinding time and the drying time, and it is concluded that samples basically displayed pure monoclinic structure when they were grinded for 20min and dried at 120°C for 8h. According to Pauling rule, it's necessary for Zn²⁺ to be enclosed by oxygen anion, the characteristic peak at 505 cm⁻¹ may correspond to Zn-O bond, and the result is consistent with the literature. Comparing to the pure BiVO₄, Zn-doped BiVO₄ shows greatly enhanced photocatalytic degradation efficiency.

ACKNOWLEDGMENT

This work was financially supported by scientific research project of Huzhou University (2015XJKY31).

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