

# Preparation and Activities of Visible-Light-Driven BiVO<sub>4</sub> doped Mn<sup>2+</sup> via Solid State Method

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**Abstract**—Using the Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, NH<sub>4</sub>VO<sub>3</sub> and 50% Mn(NO<sub>3</sub>)<sub>2</sub> solution as raw materials, the novel Mn<sup>2+</sup>-doped BiVO<sub>4</sub> photocatalysts was successfully prepared by a low-temperature grinding synthesis. And characterized by X-ray diffraction(XRD) and scanning electron microscope(SEM). The Methyl Orange (MO) was simulated as the degradation material under the visible light for studying the influence of the amount of photocatalyst and the illumination time. The visible-light absorption scope of BiVO<sub>4</sub> was broadened by doping Mn<sup>2+</sup>, the UV-Visible absorption edge was slightly red shifted and the band gap got narrowed comparing with the pure BiVO<sub>4</sub>. The results indict that the photocatalytic activities of Mn<sup>2+</sup>/BiVO<sub>4</sub> were improved comparing with the pure BiVO<sub>4</sub>. The possible reason of enhanced photocatalytic activities was discussed.

**Keywords**—BiVO<sub>4</sub>; Mn<sup>2+</sup>; Doped; Photocatalysis; Solid State Grinding Method

## I. INTRODUCTION

In recent years, photocatalytic technology has become a hot topic that is promising for the photocatalytic degradation of organic pollutants in industrial waste water by utilizing semiconductor materials. TiO<sub>2</sub> is widely used as a photocatalyst. However, its large band-gap energy of 3.2 eV has high energy demands of excitation light, causing their poor utilization of photocatalytic activity. BiVO<sub>4</sub> has received much attention for its advantages of simple preparation, poisonousless, good photodegradation efficiency<sup>[1-2]</sup>. BiVO<sub>4</sub> is an ideal photocatalysis material in response to visible-light with a direct band gap of 2.4 eV, which is very close to the center of the solar spectrum, and the absorption band edge extends up to about 520 nm. Its apparent color is orange. BiVO<sub>4</sub> possesses a conduction band potential (0 V) with a easy compound of Photo-generated carriers, as well as a poor performance on the adsorption of reactant, activity of visible light can not be utilized fully<sup>[3]</sup>. Band was adjusted by doping some metallic elements to BiVO<sub>4</sub> so as to improve its photocatalytic activity. Currently, the preparation methods of BiVO<sub>4</sub> are solid state reaction method<sup>[4]</sup>, hydrothermal method<sup>[5]</sup>, liquid precipitation method<sup>[6]</sup>, impregnation method<sup>[7]</sup>, sol-gel method<sup>[8]</sup>, microemulsion method<sup>[9]</sup> and sonochemical method<sup>[10]</sup>.

So far, extensive reviews and reports are devoted to the modification and preparation of BiVO<sub>4</sub>, the majority methods are hydrothermal method and precipitation method by doping metals such as Cu, Ag, Pt, Co. The experiment studies the preparation and photocatalytic activity of Mn<sup>2+</sup>-doped BiVO<sub>4</sub>, there is no reports about modification of BiVO<sub>4</sub> by doping Mn, Fe, Co and Ni. Positive ideas and bold innovation were devoted to explor the impact of new elements on the photocatalytic activity of BiVO<sub>4</sub> that use Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, NH<sub>4</sub>VO<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O as raw materials. The desired monoclinic BiVO<sub>4</sub> was prepared by a solid-state method by manipulating the amount of Cu(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O and grinding a certain time. The samples prepared were characterized firstly to determine whether Mn ions were successfully doped according to XRD spectrum. Secondly, the samples were characterized by using the degradation of methyl orange to calculate the degradation for studying the photocatalytic activity. The experiment possesses advantages of simple method, easy operation, obvious effect and small environmental pollution.

## II. EXPERIMENTAL PROCEDURE AND CHARACTERIZATION

### A. Preparation of Mn doped BiVO<sub>4</sub> samples

Weigh a certain amount of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and NH<sub>4</sub>VO<sub>3</sub>, then uniformly mix into an agate mortar, and different doses of Mn<sup>2+</sup> were added in proportion into it. It was grinded fully until that red-brown slurry liquid was formed. Samples were removed into a crucible after grinded and dried in a drying cabinet at 120 °C for 12 h. After the reaction, the product was removed and washed by deionized water and absolute ethanol for three times, respectively. Then the product was dried in vacuum at 60 °C for 4 h so as to obtain Mn/BiVO<sub>4</sub>. For comparative purposes, we need to prepare a blank sample. Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and NH<sub>4</sub>VO<sub>3</sub> were mixed with same doses and grinded until it was orange yellow. It was dried at 120 °C for 12 h to get rid of adsorbed water and partial crystalline water during reaction. Finally, it was dried in a drying cabinet at 60 °C for 4 h so as to obtain BiVO<sub>4</sub> samples.

### B. Characterization of Mn doped BiVO<sub>4</sub> samples

Samples were analyzed by powder X-ray diffraction by X-D6 diffractometer in this experiment. Test conditions: using Cu target (Cu K $\alpha$ ,  $\lambda=0.15406\text{nm}$ ), the accelerating voltage and the applied current were 36 kV and 20 mA, respectively. Using solid-state detector in the range of 15°~65°, the energy window ranges 1.72 V ~ 1.94 V, covering the wavelength range of Cu K $\alpha_1$ . The morphology of as-prepared Mn-BiVO<sub>4</sub> samples was characterized by S-3400N scanning electron microscope. Using ultraviolet–visible diffuse reflectance spectra (UV-vis 5A2PO54001), a scan rate of 4500 nm/min, samples were taken at an interval time of 1 min. The infrared spectrum was tested (KBr squash method) by fourier transform infrared spectrometer with the type of USA thermoelectric (NICOLET5700x).

### C. Photocatalysis experiment

10 ml of 10 mg/L methyl orange solution was added into a certain amount of Mn/BiVO<sub>4</sub> photocatalyst, in order to prevent the agglomeration of catalyst, catalyst powder was uniformly dispersed in simulated wastewater after 1-2 min of ultrasound. The above solution was placed under visible light after preheating 30 min, the reaction can be regulated. The solution was transferred into a centrifuge tube after reaction and centrifuged 30 min with a speed of 3000 rpm, then the supernatant was absorbed with plastic dropper and the absorbance was measured at  $\lambda=554\text{ nm}$ . The degradation rate was calculated according to Lambert–Beer law.

## III. RESULTS AND DISCUSSION

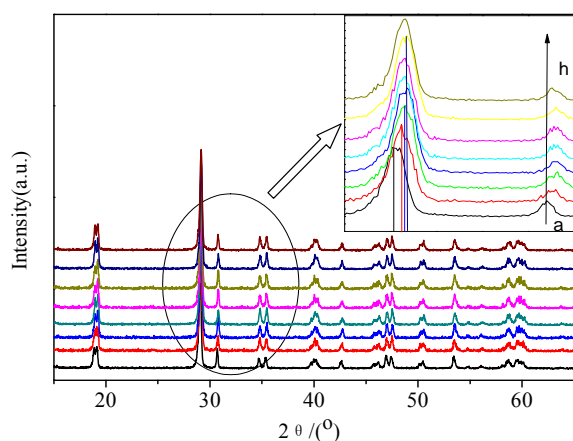


Figure 1. XRD patterns of BiVO<sub>4</sub> samples with different Mn<sup>2+</sup> doping amount. (a: pure BiVO<sub>4</sub>; b: 0.20 mL; c: 0.25mL; d: 0.30 mL; e: 0.35 mL; f:0.40 mL; j: 0.50 mL; h: 0.60 mL).

### A. Effects of doping amount for crystal type

As is shown in Fig. 1, contrast to standard cards(JCPDF: 14-0688), the crystal face index of main peak for monoclinic BiVO<sub>4</sub> is (-121) at 28.822 °, the second strong peak is (121) at 28.947 ° which sample is increased with Mn<sup>2+</sup> doping amount, and apparently moves to the small angle. It is indicated that the value of crystal plane spacing *d* is bigger according to Bragg equation, indirectly illustrating the distortion of crystal lattice that

has taken place in presence of Mn elements. The structures of sample belong to monoclinic system according to the XRD patterns which is shown in Fig .3-1, and the sample is calculated the crystal plane parameters: *a*=5.195nm, *b*=11.701 nm, *c*=5.092 nm. Its morphology is a shape of particles.

### B. Effects of doping amount for crystal morphology

As is shown in Fig. 2, the morphology of the as-prepared samples was rice-like shapes with uniform size of particle. The size of particle in blank BiVO<sub>4</sub> samples was about 500 nm and it does not agglomeration. We can see from the picture that its morphology is irregularly spherical, namely oval shape. And the growth of particle size is not consistent in all directions. Thus, the morphology of samples is similar to the uniform size of particle, which is obtained by a low-temperature solid phase grinding method, and no agglomeration.

Fig. 3 represents the SEM photograph and magnifies image of BiVO<sub>4</sub> with doping 0.25 mL of Mn<sup>2+</sup>. It can be seen that the particle size is small and uniform. The photograph in the left top was magnified tenfold, we found the surface of samples was irregular and its particles were rice-like shapes. Thus, the morphology of samples was similar to the uniform size of particle, which is obtained by a low-temperature solid phase grinding method, and no agglomeration. It is the result of XRD according to the calculation of grain.

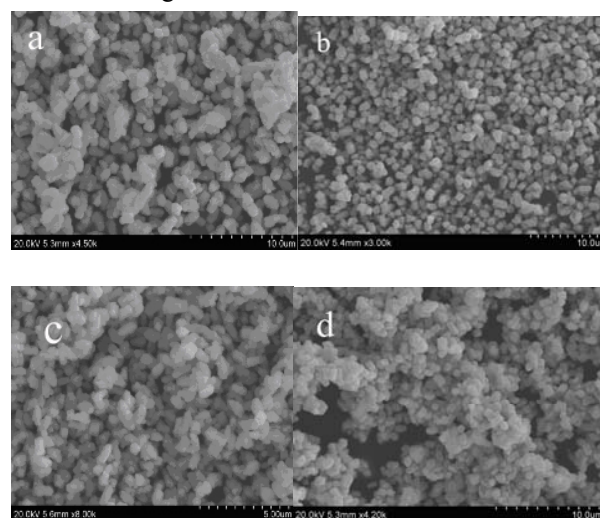


Figure 2. SEM images of the samples. (a: pureBiVO<sub>4</sub>, b:0.20mLMn<sup>2+</sup>/BiVO<sub>4</sub>, c:0.30mLMn<sup>2+</sup>/BiVO<sub>4</sub>, d:0.60mLMn<sup>2+</sup>/BiVO<sub>4</sub>).

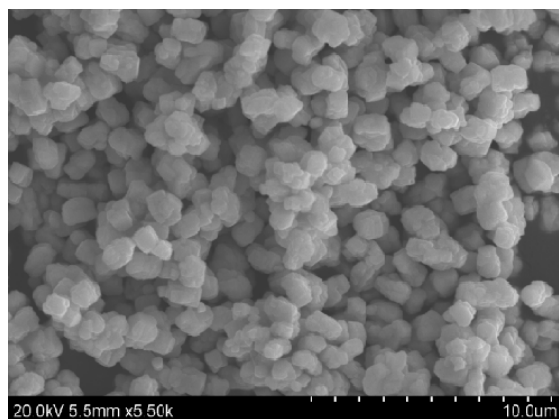


Figure 3. SEM image of BiVO<sub>4</sub> with doping 0.25 mL of Mn<sup>2+</sup>.

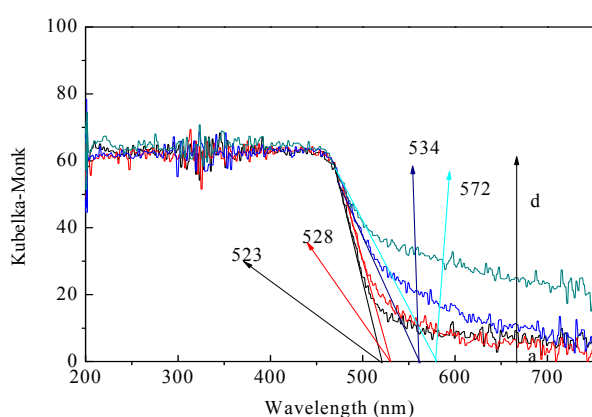


Figure 4. Diffuse reflectance spectra of different Mn<sup>2+</sup> doped solid sample powder by Kubelka-Monk function transformation (a: pure BiVO<sub>4</sub>; b: 0.2 mL Mn<sup>2+</sup>; c: 0.4 mL Mn<sup>2+</sup>; d: 0.5 mL Mn<sup>2+</sup>)

### C. Effects of doping amount for diffuse reflectance properties.

Upon the UV-vis diffuse reflectance spectra (Fig. 4), the doping amount of Cu<sup>2+</sup> has an apparently effect on photo absorption properties of solid sample powder. First, the curve after doping Mn possesses obvious absorption edges and an extensive range of spectral response comparing with pure BiVO<sub>4</sub>. Especially, it is in the Visible-light area upon 400 nm with a big difference of photo absorption. Second, comparing to pure BiVO<sub>4</sub>, the doping concentration also has a significant effect on the absorbance of the sample. By using tangent method, 0.2 mL of Mn<sup>2+</sup>/BiVO<sub>4</sub>, 0.4 mL of Mn<sup>2+</sup>/BiVO<sub>4</sub> and 0.5 mL of Mn<sup>2+</sup>/BiVO<sub>4</sub> were obtained, the corresponding wavelength of absorption edge were 528 nm, 534 nm and 572 nm, respectively. On the basis of  $E_g = 1240/\lambda_g$ , the value,  $E_g$  (a)=2.37 eV,  $E_g$  (b)=2.35 eV,  $E_g$  (c)=2.32 eV,  $E_g$  (d)=2.12 eV obtained indicate that the energy gap existing certain fluctuation is decreased (i.e., red shift) first, and then increased (i.e., blue shift) with Cu<sup>2+</sup> content, which is smaller than be reported in similar literatures.

### D. Effects of doping amount for photocatalytic activities

Taking the appropriate concentration of methyl orange (MO) to simulate the required degradation of wastewater, while the appropriate quality of samples was added into it

for the experimental study of photocatalytic degradation. A certain amount of the sample was added into 10 mL of MO solution, after 2 min of ultrasonic homogenization, the mixture was magnetically stirred for a certain time under preheated 150 W visible light, then removed to a dried centrifugal tube with a speed of 3000 r/min and taken after centrifugation of 30 min. Supernatant (approximately 2/3) was taken out with a dropper and transferred to another centrifugal tube, and then centrifuged for 30 min. Upon completion of above steps, supernatant was taken for the measure of absorbance at 752 UV spectrophotometer (MO  $\lambda_{max}$ =464 nm) by recording the absorbance value of mixture solution at the maximum absorption peak of 464 nm.

Fig. 5 represents the Effects of the absorbance of methyl orange with different Mn<sup>2+</sup> concentrations of sample. a represents the absorbance curve of pure BiVO<sub>4</sub> samples, b represents the absorbance curve of Mn<sup>2+</sup>/BiVO<sub>4</sub> samples with doping 0.2 mL of Mn<sup>2+</sup>. c represents the absorbance curve of Mn<sup>2+</sup>/BiVO<sub>4</sub> samples with doping 0.4 mL of Mn<sup>2+</sup>. d represents the absorbance curve of Mn<sup>2+</sup>/BiVO<sub>4</sub> samples with doping 0.5 mL of Mn<sup>2+</sup>. It can be seen from the graph, the amount of catalyst is the key factor in determining its photocatalytic reaction. Generally, the degradation rate is decreased with the increase of the content. Moreover, the gap between samples with different photocatalytic properties will gradually reflect, even enlarge. It is obvious that with the increase of the Cu content, the MO concentration is decreased largely under the same amount. With 10 mg as an example, 25 mg of Mn<sup>2+</sup>/BiVO<sub>4</sub> samples compared to BiVO<sub>4</sub> samples, the residual MO concentration was demonstrated that the former to the latter was 80 % after photocatalysis.

Fig. 6 represents the effects of samples with different contents of Mn<sup>2+</sup> on the absorbance of methyl orange with different photocatalytic time of sample. a represents the absorbance curve of pure BiVO<sub>4</sub> samples, b represents the absorbance curve of Mn<sup>2+</sup>/BiVO<sub>4</sub> samples with doping 0.2 mL of Mn<sup>2+</sup>. c represents the absorbance curve of Mn<sup>2+</sup>/BiVO<sub>4</sub> samples with doping 0.4 mL of Mn<sup>2+</sup>. d represents the absorbance curve of Mn<sup>2+</sup>/BiVO<sub>4</sub> samples with doping 0.5 mL of Mn<sup>2+</sup>. It can be seen from Fig.3-5 that the absorbance of methyl orange is declining increased with extending of irradiation time under a certain range of irradiation time, and the decrease is relatively obvious. It also illustrates that the degradation rate of catalysts is increasing, but when irradiation time is longer than 120 min, the decline of absorbance becomes smaller and even stops at a certain value rather than continues to decline. In the same way, we can conclude that the degradation rate of catalysts with equivalent mass gets better due to Mn element. The catalytic effect of 0.5 mL of Mn<sup>2+</sup>/BiVO<sub>4</sub> samples with a catalytic time of 60 min is similar to reaction time of 120 min.

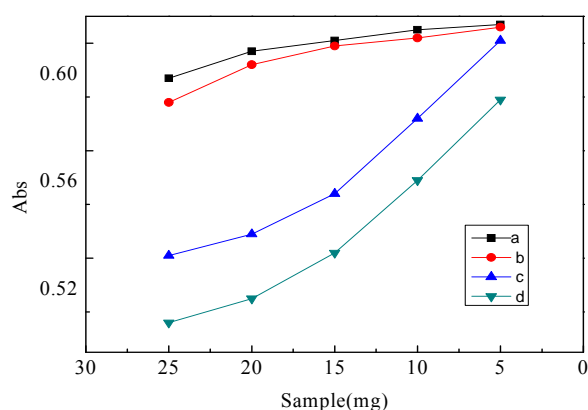


Figure 5. Effects of the absorbance of methyl orange over different  $\text{Mn}^{2+}$  concentration of sample. (a: pure  $\text{BiVO}_4$ ; b:  $0.2 \text{ mL Mn}^{2+}/\text{BiVO}_4$ ; c:  $0.4 \text{ mL Mn}^{2+}/\text{BiVO}_4$ ; d:  $0.5 \text{ mL Mn}^{2+}/\text{BiVO}_4$ ).

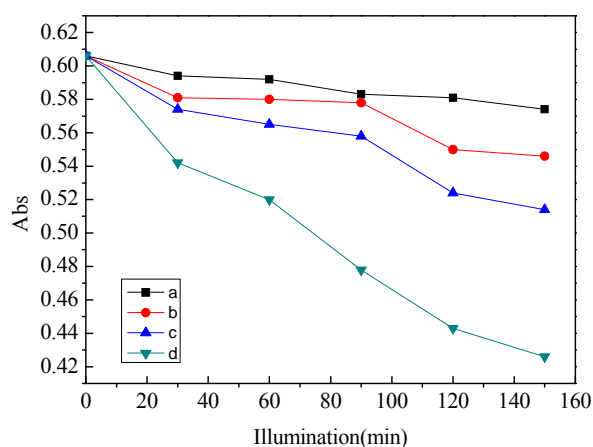


Figure 6. represents the effects of samples with different contents of  $\text{Mn}^{2+}$  on the absorbance of methyl orange with different photocatalytic time of sample. (a: pure  $\text{BiVO}_4$ ; b:  $0.2 \text{ mL Mn}^{2+}/\text{BiVO}_4$ ; c:  $0.3 \text{ mL Mn}^{2+}/\text{BiVO}_4$ ; d:  $0.5 \text{ mL Mn}^{2+}/\text{BiVO}_4$ )

#### IV. CONCLUSION

Using the  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{NH}_4\text{VO}_3$  and  $\text{Mn}(\text{NO}_3)_2$  as raw materials, the as-prepared Mn-doped  $\text{BiVO}_4$  photocatalysis are nanometer-sized. The result indicates that samples are basic monoclinic phases when grinded about 20 min and dried at  $115^\circ\text{C}$ . The as-prepared Mn doping  $\text{BiVO}_4$  catalyst in response to visible light has enhanced compared to pure  $\text{BiVO}_4$ .

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