

Preparation and Photocatalytic Activities of Fe/BiVO₄ by Low-Temperature Solid State Method

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Abstract—Fe/BiVO₄ photocatalyst was synthesized via a low-temperature solid state method by using the Bi(NO₃)₃·5H₂O, NH₄VO₃ and Fe(NO₃)₃·9H₂O as starting materials. And X-ray diffraction (XRD), Scanning electron microscopy (SEM), Infrared spectroscopy (FT-IR) and Ultraviolet-visible diffuse reflectance spectra (UV-VIS DRS) were used to characterize the as-synthesized Fe/BiVO₄. The photocatalytic degradation experiment was carried out by the Methyl Orange (MO) simulated as the polluted water. Then we discussed the influence of reaction time and the mass of photocatalyst to investigate photocatalytic activity of Fe/BiVO₄ sample under light. It was demonstrated that the as-synthesized Fe/BiVO₄ showed a sheltie structure with monoclinic system whose diameter was about 400 nm~1500 nm. Furthermore, the ability of light absorption could be heightened by doping Fe³⁺ to induce much better photocatalytic performance. In doping process Fe³⁺ may be the first replacement with V⁵⁺ in the crystal and at the second step Fe³⁺ was substitute for Bi³⁺. The increase of Fe³⁺ content led to narrows of the band gap, red shift, the absorption edge and raises of photocatalytic degradation ability.

Keywords—low-temperature solid state; Fe/BiVO₄; photocatalysis; methyl orange; doped

I. INTRODUCTION

Recently the semiconductors as photocatalysis were widely applied in splitting water to produce hydrogen [1], degradation of organic pollutants [2], carbon capture and sequestration [3] and photoelectrochemical cell research [4]. Titanium dioxide (TiO₂) is an industrially important product, for example P25, however wide-band gap semiconductor always suffers from higher energy excited by UV-light [1-4], not adequately use sunlight. So face this trouble, except use of nanometer-structures and element doping[5], some new types photocatalyst had been utilized and investigated as BiVO₄[6], BiFeO₃[7], Bi₂WO₆[8], ZnWO₄[9] and Cu₂O[10]. Bismuth(III) metavanadate (BiVO₄) was narrow-band gap semiconductor materials on that presents interesting technological properties, especially photocatalytic activity and monoclinic BiVO₄ had better than tetragonal[11]. The photocatalytic performance of BiVO₄ depended strongly on the crystalline phase and morphological characteristics, which

had effect from preparation method as direct precipitation method [12], microwave method [13], hydrothermal method [14], dipping method [15], Sol-gel method [16]. Resulting from the slow electron-hole separation rate and the fast electron-hole recombination rate in the BiVO₄ surface, metal doping may overcome low conversion efficiencies. These noble metal nanoparticles (NPs) had play on serving as electron sinks and to facilitate interfacial electron transfer, but large NPs may also consume holes, thus serving as recombination centers. In fact some kinds of metal-loaded visible-light-driven photocatalysis were synthesized, as Mo-BiVO₄ [17], Ag-BiVO₄ [17], Pd/BiVO₄ [18], Cu-BiVO₄ [19], Ni-BiVO₄ [20], Au/BiVO₄ [21] and the metals existed as oxides on the surface of the particles. These powders had better degradation rate than that of pure BiVO₄, probably due not only a decrease of energy band gap and isoelectric point, but also the augmentation of surface absorption. The later plays more important roles in visible-light region. Meanwhile in these papers, the frequency of “load” was higher than that of dope word, which means doping successful or not is an event worth considering. Moreover, the mostly catalysts preparation progress referred to oxide and reduction reaction, in which the mass of element doping or metal oxide cannot be precisely controlled. To solve this problem, metal doping were synchronized with preparation of BiVO₄ in one-pot by low-temperature solid state method which had advantages of simple reaction conditions and easy control of process parameters.

II. EXPERIMENTAL AND CHARACTERIZATION

A. Synthesis of Fe/BiVO₄ Selecting a Template

2.425 g Bi(NO₃)₃·5H₂O, 0.5849 g NH₄VO₃ and 5 mg Fe(NO₃)₃·9H₂O were mixed evenly in a mortar, grinding until to reddish brown paste liquid generation. The red brown paste liquid was transferred to the ceramic crucible under 120 °C for 24h. The powders was washed twice by distilled water and ethanol, and then put into oven for drying. At last the product was label with 0.3wt % Fe/BiVO₄. Repeat the above steps, while the grinding time kept on the same, 0 wt %, 0.6 wt%, 1.2 wt%, 1.8 wt%, 2.4 wt%, 3.0 wt% and 3.6 wt% Fe/BiVO₄ had got.

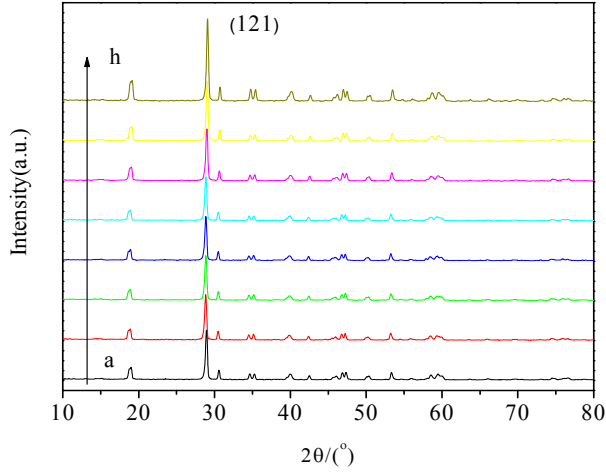


Figure 1. XRD patterns of various BiVO_4 (a: pure BiVO_4 ; b: 0.3 wt%; c: 0.6 wt%; d: 1.2 wt%; e: 1.8 wt%; f: 2.4 wt%; g: 3.0 wt%; h: 3.6 wt%)

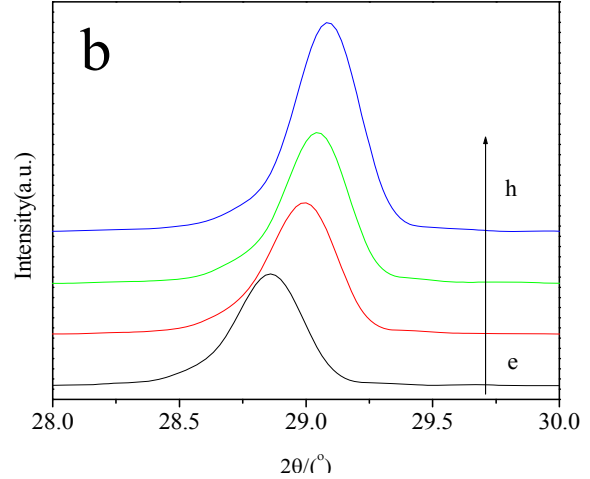


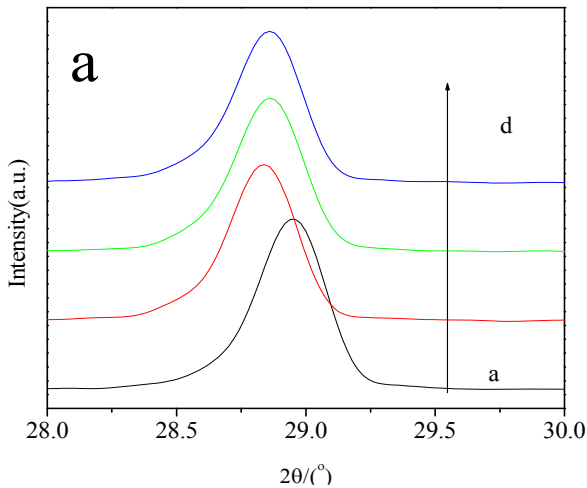
Figure 2. XRD Partial enlarged drawings of various BiVO_4 in (121) (a: pure BiVO_4 ; b: 0.3 wt%; c: 0.6 wt%; d: 1.2 wt%; e: 1.8 wt%; f: 2.4 wt%; g: 3.0 wt%; h: 3.6 wt%)

B. Characterization of Fe/BiVO_4

X-ray diffraction (XRD) patterns of the dry powders were characterized on a DX-60 diffractometer (Puxi, China) with a slit of $1/2^\circ$ at a scanning speed of 4°min^{-1} using $\text{Cu K}\alpha$ radiation. Samples for scanning electron microscopy (SEM) analysis were carried out by S-3400N (Hitachi, Japan) and operated at 15.0 kV. The diffuse reflectance spectra (DRS) of the samples and the UV/Vis absorption spectra of the MO solutions were obtained with a Thermo Fisher Scientific 5A2PO54001 UV/Vis spectrophotometer at speed of 450 nm min^{-1} .

C. Photocatalytic experiments of Fe/BiVO_4

Photocatalytic activities of as-prepared samples were evaluated by the degradation of 10 mg/L MO, the catalyst was added into 10 mL of MO, after ultrasound for 3 min, (then) the solution was irradiated under the HQL-BT metal halide light source of Germany Osram Company for 20-160 min, then (after that) the absorbance was measured from the supernatant liquor. The fade rate of methyl orange was measured by the linear curve of the standard absorbance about MO concentration or used by the Lambert–Beer law.



III. RESULTS AND DISCUSSION

A. The effect of Fe amount in crystal structure

The curves in Fig. 1 presented the XRD pattern of samples with different mass Fe. That was consistent with the standard characteristic peaks of monoclinic BiVO_4 (JCPDF: 14-0688) at (110), (011), (-121), (121), (040), (200) and (002). In spectrum these sharp peaks means high diffraction intensity which showed that the samples had good crystal type. And these diffraction peaks position, along the X coordinate, regular occurred in small shift which was show the rule associated with Fe amount. In Fig. 2a and 2b, the peak of (121) appeared “red shift” and “blue shift” accompanied by Fe amount

In Fig. 2a, the peak shift of modified BiVO_4 was trend to left or to reduce the diffraction angle with 0 wt% to 1.2 wt% of Fe in samples. According Bragg equation ($2d\sin\theta=n\lambda$), with the decrease of diffraction angle, interplanar distance increased, probably resulting from distortion of lattice including Fe^{3+} displacement of vacancies or V^{5+} in crystal BiVO_4 , because the radiuses of Fe^{3+} and V^{5+} were respectively 0.064 nm and 0.054 nm. But from 1.8 wt% to 3.6 wt%, the change tendency of diffraction angle made the turn. Obviously, the interplanar distance decreased because at the second step Fe^{3+} was substitute for Bi^{3+} which radius was 0.103 nm.

B. The effect of Fe amount in morphology

Fig. 3 represents the SEM images of various BiVO_4 samples. The monoclinic morphological structures were clearly confirmed. The four concentration samples shows that morphological nanoparticles or micro particles with a size of about 400-1500 nm, and the size of 3.6 wt% catalyst was the smallest about 400 nm in Fig. 3d. These particles had good dispersion, no obvious aggregation.

C. Photophysical Properties and Photocatalytic Activity of Fe/BiVO₄

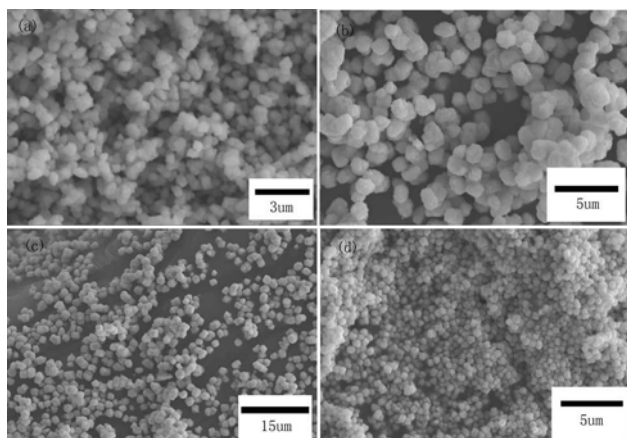


Figure 3. SEM images of various BiVO₄(a: 0.3 wt%; b: 1.2 wt%; c: 1.8 wt%; d: 3.6 wt%)

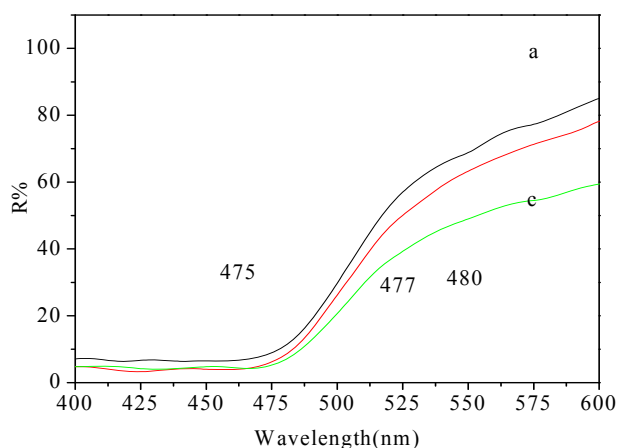


Figure 4. Diffuse reflectance spectra of various BiVO₄. (a: 0.6 wt%; b: 1.8 wt%; c: 3.6 wt%)

Fig.4 represents the diffuse reflection spectra (DRS) of 0.6 wt% Fe/BiVO₄, 1.8 wt% Fe/BiVO₄, and 3.6 wt% Fe/BiVO₄. The former two samples possess an absorption band from 470 to 520 nm, whereas 3.6 wt% Fe/BiVO₄ shows one from 480 to 520 nm. The absorption edges of three kinds of BiVO₄ show a steep edge, indicating that visible-light absorption is attributed to the band gap transition rather than the transition from an impurity level [22]. According to DRS, the band gaps (E_g) were calculated to be 2.61, 2.60, and 2.58 eV for 0.6 wt%, 1.8 wt% and 3.6 wt%. so with the increase of Fe³⁺ content in the samples, the absorption edge shifts gradually increased, and band gap was gradually narrow which was result in an enhancement of catalytic performance.

In Fig. 5 under visible light MO absorption decreased with irradiation time over 10 mg of Fe/BiVO₄ which concentration were 0 wt % to 3.6 wt% with curves a to h. In general, the content of Fe³⁺ in the sample was higher, the lower the absorbance of the methyl orange solution more quickly at the same irradiation time. It suggested that Fe³⁺ could effectively enhance the photocatalytic

performance of BiVO₄. In addition, increasing illumination time, the absorbance of the MO solution would decrease, especially the decline of absorbance by as much as 23.23% of 3.6 wt% Fe/BiVO₄ for 90 min~120 min. From Fig. 6, the content of Fe³⁺ in the sample was higher, the lower the absorbance of the methyl orange solution the more quickly at the same mass. It also proved that Fe³⁺ could effectively enhance the photocatalytic performance of BiVO₄ and Fe/BiVO₄. Otherwise, the mass of samples had great effect on degradation rate of MO, and there was (the) best choose at 15 mg for 3.6 wt% Fe/BiVO₄, when it enhanced 1 times than pure BiVO₄ in fade rate from 21.3% to 47.7%. As reported [20], The Ni oxide as P type semiconductor was dispersed in the surface of N type semiconductor BiVO₄ to form composition of P-N heterojunction. The P-N heterojunction could effectively separate the photogenerated carrier, and greatly improve the catalytic performance of sample. And Fe and Ni located in the same fourth period VIII group, their chemical properties were very similar, so the performance of BiVO₄ load Fe was better than pure BiVO₄.

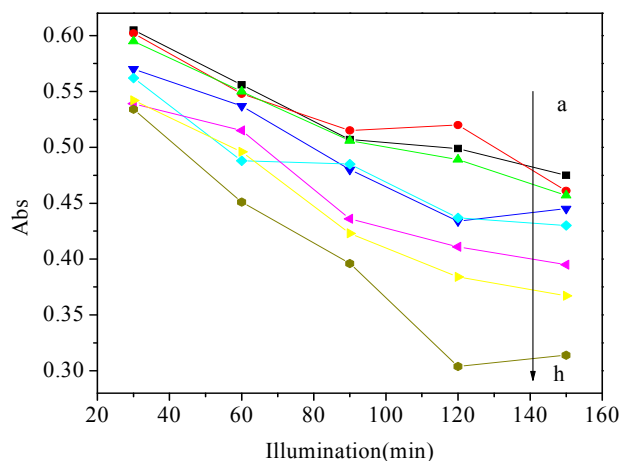


Figure 5. Decrease in MO absorption of irradiation time over 10mg of Fe/BiVO₄ under visible light ($\lambda > 420$ nm).(a: pure BiVO₄; b: 0.3 wt%; c: 0.6 wt%; d: 1.2 wt%; e: 1.8 wt%; f: 2.4 wt%; g: 3.0 wt%; h: 3.6 wt%)

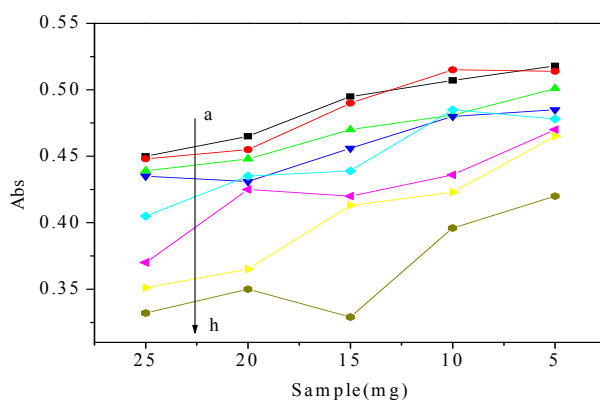


Figure 6. Decrease in MO absorption of irradiation mass over Fe/BiVO₄ under visible light for 90 mins ($\lambda > 420$ nm).(a: pure BiVO₄; b: 0.3 wt%; c: 0.6 wt%; d: 1.2 wt%; e: 1.8 wt%; f: 2.4 wt%; g: 3.0 wt%; h: 3.6 wt%)

IV. CONCLUSION

Fe/BiVO₄ samples containing different Fe³⁺ amount was prepared by low temperature solid phase reaction. In doping process Fe³⁺ may be the first replacement with V⁵⁺ in the crystal, and at the second step Fe³⁺ was substitute for Bi³⁺ with Fe amount further increase. The increase of Fe³⁺ content led to narrows of the band gap, red shift the absorption edge and raises of photocatalytic degradation ability.

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