# Preparation and Activities of Visible-Light-Driven BiVO<sub>4</sub> by Doping Ni via Solid State Method

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Abstract—Using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and NH<sub>4</sub>VO<sub>3</sub> as raw materials, Ni-doped BiVO<sub>4</sub> photocatalysts with monoclinic scheelite were prepared by a lowtemperature grinding method. The physical and optical properties of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-VIS diffuse reflectance spectroscopy (DRS), and the chemical bond of the samples was analyzed by Infrared spectroscopy (FT-IR). The Methyl Orange (MO) was simulated as the sewage under the condition of visible light for studying the influence of the amount of photocatalyst and the illumination time. The results showed that the visiblelight absorption scope of BiVO<sub>4</sub> was broadened by doping Ni and the catalytic effect was enhanced comparing with the pure BiVO<sub>4</sub>. The degradation rate of as-prepared samples was up to 90% with 10mg and 20mg Ni and photocatalytic time of 90 min.

*Keywords- BiVO<sub>4</sub>*; *solid state method*; *Ni-doped*; *photocatalysis*; *methyl orange* 

## I. INTRODUCTION

The composite oxides of Bi were interested by many researchers and BiVO4 had a promising future about photocatalytic material for narrow energy gap, strong oxide and reduce, low cost, no toxicity and excited by visible-light[1]. It had three crystal phases of tetragonal zircon (2.9 ev), monoclinic scheelite (2.4 ev) and tetragonal scheelite (2.4 ev), and the monoclinic scheelite structure showed the best photocatalytic performance than those of another two crystalline forms under visible-light illumination[2-3]. The photocatalytic property of BiVO4 was strongly dependent on its morphology, size and crystalline forms, which were mainly effected by methods, for example, impregnation [3], microwave-hydrothermal synthesis [4], sol-gel [5] and low-temperature solid state method [6]. However, with the conduction band potential of 0V and high recombination rate of electron-hole, BiVO<sub>4</sub> possesses poor absorbance and low efficiency of photocatalytic oxidation. It is necessary to dope certain material as electron acceptor to reduce the possibility of generation of photo electron and recombination of electron-hole. Finally, the photocatalytic activity of novel samples is highly improved. Up to now, there are most

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reports on development of doping  $BiVO_4$  with metals such as Cu[7], Ag[8], Pt[9] and Co[10] mainly by means of hydrothermal method or precipitation procedure.

Basing on previous reports, using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and NH<sub>4</sub>VO<sub>3</sub> as raw materials, Ni-doped BiVO<sub>4</sub> photocatalysts with monoclinic scheelite were prepared by a low-temperature grinding method and the preparation and activities of novel photocatalyst, Ni/BiVO<sub>4</sub>, were studied in this work. Testing the existence of Ni element by XRD, observing the morphology of samples by scanning electron microscopy (SEM), analyzing the formed chemical bond by Infrared spectroscopy (FT-IR) and characterizing the optical properties of samples by UV-VIS diffuse reflectance spectroscopy (DRS). And the photocatalytic activities of samples were studied by degrading methyl orange (MO) and calculating the degradation rate.

## II. EXPERIMENTAL

### A. Synthesis of Ni/BiVO<sub>4</sub> samples

In this work, the synthesis of Ni/BiVO<sub>4</sub> was shown in the following way: 5.0 mmol (2.425 g) Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, 5.0 mmol (0.585 g) NH<sub>4</sub>VO<sub>3</sub> and corresponding Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were uniformly mixed and fully grinded in agate mortar for 30min, then mixture turned to be the 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, the product was added into centrifuge tube and washed with distilled water and anhydrous alcohol for two times and one time, respectively. After centrifuged, the as-obtained substance was again transferred to a crucible and dried in an oven at 60°C for 4h then Ni/BiVO<sub>4</sub> samples were prepared. Blank experiment also was carried out to well compare the superiority of novel samples, in which mixing and grinding same Bi (NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and NH<sub>4</sub>VO<sub>3</sub> for 30min then the color of mixture entirely transformed into orange syrup and pure BiVO<sub>4</sub> sample was obtained by same procedure as the measures above mentioned.

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

The XRD patterns of samples were obtained on an X-D6 equipment with Cu K $\alpha$  radiation ( $\lambda$ =0.15406 nm) and

the operating condition was as follows: the tube voltage was 36kV, the applied current was 20mA, the scanning ranges were  $15^{\circ}$ ~ $65^{\circ}$ . Morphology characteristics of asprepared samples were characterized by scanning electron microscopy (S-3400N). A UV–vis spectrophotometer (5A2PO54001) was used to obtain the absorption spectra of samples, which works at a scan rate of 4500 nm/min and sample every two minutes. And Infrared spectroscopy analysis (KBr squash method) was performed on Fourier transform infrared spectroscopy (NICOLET5700x, Thermo Electron)

### C. Photocatalytic activity of Ni/BiVO<sub>4</sub> samples

0.01g Ni/BiVO<sub>4</sub> catalysts were added into 10mL methyl orange solution (10mg/L) simulated as the sewage, in which photocatalyst powder was uniformly dispersed by ultrasonic probe for 1-2min, 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 the wavelength of 554 nm, and the degradation rate was calculated by the Lambert–Beer law.



III. RESULTS AND DISCUSSION

Figure 1. XRD patterns of Ni/BiVO<sub>4</sub> with different contents of Ni; a: pure BiVO<sub>4</sub>; b: 5 mg Ni; c: 10 mg Ni; d: 20 mg Ni; e: 30mg Ni; f: 50mg Ni.

## A. X-ray diffraction

Although tetragonal and monoclinic scheelite structures possess particular similar crystal structure and band gap (2.4 eV), their lattice parameters are not totally identical which may lead to serious distortion of Bi-O polyhedron in monoclinic scheelite structure and higher photocatalytic activity of monoclinic scheelite BiVO<sub>4</sub>. In the structure of monoclinic scheelite BiVO<sub>4</sub>, Bi combined with O and formed regular octahedron. In addition, V existed in the structure by the form of VO<sub>4</sub> tetrahedrons that didn't contact with each other. As well as we know, monoclinic scheelite structures belong to ABX4 type of monoclinic system, and the radius of  $Bi^{3+}$ ,  $V^{5+}$  and  $Ni^{2+}$  are 0.103nm, 0.054nm and 0.069nm, respectively. According to the PDF card of as-prepared pure BiVO<sub>4</sub>, its lattice

parameters (a=5.195Å, b=11.701Å and 5.092Å, α=90°,  $\beta$ =90.38° and  $\gamma$ =90°) were obtained. Regardless of the kind of material as source of Ni dopant, it is necessary to induce defect reaction for keeping electroneutrality. BiVO<sub>4</sub> was found to mainly exist in three crystalline phases and the monoclinic scheelite structure showed the best photocatalytic performance than those of another two crystalline forms. Therefore, many synthesis methods have been focused on the selective preparation of scheelitemonoclinic BiVO<sub>4</sub> photocatalyst. The XRD patterns of samples with different contents of Ni as is shown in Fig. 1. It was worth noting that all samples had the double peaks (corresponding to  $19.0^{\circ}$ ,  $35.0^{\circ}$  and  $47.0^{\circ}$ ) which symbolized the monoclinic scheelite structure and high crystallinity, as well as those matched well with the standard card (JCPDS14-0688). Above mentioned indicated that crystal structure of BiVO<sub>4</sub> did not change when doped BiVO<sub>4</sub> with Ni, and the expected samples were successfully prepared. However, the characteristic peaks of Ni element and its oxide derivative didn't appear in the patterns, which may be caused by the low content of Ni. The diffraction peaks began to appear the trend of left shift and diffraction angle became smaller with the increase of Ni content. We can know the lattice spacing is widen from Bragg equation and indirectly demonstrates the formation of lattice distortion by doping Ni





Figure 2. SEM micrographs of different samples: a: pure BiVO<sub>4</sub>; b: 5mg Ni; c: 10 mg Ni.

# *B.* The influence of Ni content on the morphology and size of samples.

Fig. 2 shows the SEM images of samples with different contents of Ni. The uneven distribution and apparent agglomeration of particles can be clearly observed in figure (a). Comparing three images nearly similar, although pure BiVO<sub>4</sub> sample and Ni doped BiVO<sub>4</sub> samples basically had same morphology, there are a few of grains on the surface of Ni doped BiVO<sub>4</sub> samples. The amount of loaded grains becomes larger and the agglomeration phenomenon is weakened with the increase of Ni content, which indicates the better absorption capacity in absorbing organic compounds. In general, Photo electron - hole pairs are difficult to combine when samples possess high absorption capacity. Finally, the photocatalytic activities of samples get improved.

### C. FT-IR study

Although the existence of Ni species has been indicated in XRD analysis, their specific places need to be further studied by other measures. According to Pauling rule, it's necessary for Ni<sup>+</sup> being enclosed by oxygen anion. Inspection of Fig. 3, the characteristic peak at 726 cm<sup>-1</sup> may correspond to Ni-O bond because the peak is only observed in Ni doped BiVO<sub>4</sub> samples.



Figure 3. Infrared spectra of pure and Ni doped BiVO<sub>4</sub> series samples;a: 10 mgNi; b: 5 mgNi; c: pure BiVO<sub>4</sub>



Figure 4. UV-vis diffuse reflectance spectra of different samples; a: (a: pure BiVO<sub>4</sub>; b: 30 mg Ni; c: 5mg Ni; d: 10 mg Ni.

# D. DRS analysis

The UV-vis diffuse reflectance spectra of pure and Ni/BiVO<sub>4</sub> samples are shown in Fig. 3-4 to study the effect of Ni content on band gap, which also show the absorption of different samples. After Ni species are doped, the absorption edge of the Ni/BiVO4 samples shifts to red light and the difference in visible light absorption is more obvious when the wavelength is over 500nm. The band gapes of all samples were calculated by the equation: Eg=hc/ $\lambda_0$ =1240/ $\lambda_0$ , where Eg (eV) is band gap),  $\lambda$  (mm) is the intersection between each curve and x axes. The intersections of pure BiVO<sub>4</sub>, 5 mg Ni/BiVO<sub>4</sub>, 10 mg Ni/BiVO<sub>4</sub> and 30 mg Ni/BiVO<sub>4</sub> are 556nm, 566nm and 538nm, while the values of band gap are 2.36eV, 2.36eV and 2.30eV, respectively, The band gap energy (Eg value) of pure BiVO<sub>4</sub> is slightly smaller than the reported values (2.4eV). Those can be attributed to different crystallinities and particle size of samples because experiment is conducted by hand lapping, which is difficult to reach the same grinding conditions. The band gapes of doped samples are relatively smaller comparing the pure BiVO<sub>4</sub>. And the photocatalytic activity of doped samples is improved under visible light irradiation.



Figure 5. The photodegradation of MO over Ni/BiVO<sub>4</sub> with different Ni content is displayed.



Figure 6. The degradation of MO over samples with different illumination time; a: pure BiVO<sub>4</sub>; b: 30 mg Ni; c: 50 mg Ni; d: 5 mg Ni; e: 10 mg Ni; f: 20 mg Ni.

### E. Photoactalytic activity

Fig. 5 had showed the influence of Ni content on the degradation rete of MO. The degradation rate of doped samples is greatly enhanced and becomes bigger with the increase of the quality of samples. However, the degradation rate becomes big firstly and then becomes small with the increase of Ni content. Ni/BiVO<sub>4</sub> samples with 10 mg and 20 mg Ni had the optimal and similar degradation effect, and the degradation rate of them was up to 90%. Further the original color of the two samples' solution changes to light yellow, which also shows the better catalytic effect comparing to other samples.

Fig. 6 showed the degradation rate of MO solution over Ni/BiVO<sub>4</sub> with different Ni content at different photocatalytic time, the degradation rate increased firstly then decreased with the increase of time, although the trend isn't obvious. All samples could obtain the best photocatalytic effect under visible light irradiation for 90 min. However, Ni/BiVO<sub>4</sub> samples with 10mg and 20mg Ni still possessed the optimal degradation effect and the degradation rate was nearly 90%.

After Ni was doped, the formed NiO could be considered as receptor and loaded on the surface of catalyst, which was the reason why the doped samples had improved photocatalytic activity. Therefore, the excited electron of conduction band could be captured by receptor Ni, and it was difficult to generate photo electrons and combine photo electrons with electron hole, which made doped samples exhibit enhanced quantum efficiency, great visible-light activity and high catalytic activity comparing to pure BiVO<sub>4</sub>. However, the excess Ni results in the uneven distribution of more NiO crystal particle on the surface of catalyst and the low activity. Therefore, the optimal amount of Ni could be obtained.

### IV. CONCLUSION

In this work, using the  $Bi(NO_3)_3 \cdot 5H_2O$ ,  $NH_4VO_3$  and  $Ni(NO_3)_2 \cdot 6H_2O$  as main raw materials, and nano-sized  $Ni/BiVO_4$  photocatalysts with monoclinic structure were successfully prepared by a low-temperature grinding synthesis. And these samples showed complete crystal, fine crystallinity. After Ni was doped, some particles were absorbed on the surface, which was of benefit to improve photocatalytic activity. The largest degradation rate of asprepared samples was up to 90% with 10 mg and 20 mg Ni and photocatalytic time was 90 min.

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