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Synthesized BiVO_4 was by the co-precipitation method for Rhodamine B degradation under visible light

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Abstract. Recently, BiVO_4 photocatalysts has been received much attention in field of catalysts. Because it can be used to degrade harmful organic catalysts in visible light, irradiation produces CO_2 , H_2O and less harmful organic matter. In this study, we have successfully synthesized a BiVO_4 photocatalysts via co-precipitation method in the presence of urea and different calcined temperatures. The survey calcined temperatures as 300 °C; 350 °C; 400 °C and 450 °C. The obtained materials were characterized by Scanning electron microscope (SEM) and X-ray diffraction (XRD). The photocatalytic activity was evaluated by the photocatalytic degradation of rhodamine B (RhB) degradation under visible compact Philip lamp (40W) light irradiation. The result indicates that all samples calcined are monoclinic scheelite structure of BiVO_4 . The BiVO_4 -350 °C sample performed the best in the photodegradation of RhB.

1. Introduction

The global energy crisis and environmental pollution problem resulting from rapid population growth and industrial development [1-6]. It have increased the demand for renewable energy source and environmentally friendly technologies. Especially solar energy is renewable energy source. It is widely used as Solar panel, water heating, Water treatment and Other potential. For this research, photocatalytic techniques using semiconductor materials provide an ideal solution in terms of solar conversion and removal of pollutants. There are a lot of visible-light responsive photocatalysts such as CdTe, TiO_2 , ZnO, Cu_2O , Fe_2O_3 , WO_3 , BiVO_4 , have been researchers reported [7-14].

Among them, bismuth vanadate (BiVO_4) has attracted significant interest of researchers due to its outstanding features, as resistance to corrosion, low band gap, non-toxicity and is a photocatalyst for pollutant decomposing under visible-light irradiation [15-18]. It has three crystalline phases: monoclinic scheelite (s-m) and tetragonal zircon (s-t) and tetragonal scheelite structure (z-t). However, the monocrystalline scheelite crystal has the best photocatalytic activity in the three main



crystalline structures of BiVO_4 [19-21]. At present, The BiVO_4 can be synthesized by hydrothermal, co-precipitation and metalorganic decomposition to make for fabrication of monoclinic BiVO_4 crystals [22-24]. In this study, we synthesized BiVO_4 by co-precipitation method in the presence of urea. Urea plays an important role in determining morphology, crystalline and crystalline dimensions. In this study, BiVO_4 were synthesized via a simple combination of urea assisted co-precipitation and post-calcination processes to further enhance its photocatalytic activity.

2. Materials and Methods

2.1. Materials

Bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O} \geq 98\%$); Ammonium metavanadate ($\text{NH}_4\text{VO}_3 \geq 99\%$) and Rhodamin B ($\geq 95\%$) were purchased from Sigma-Aldrich; Urea ($\text{H}_2\text{NCONH}_2 \geq 99\%$) and nitric acid (HNO_3 , 65-68%) were obtained from Xilong Chemical Co., Ltd. (China).

2.2. Synthesis of BiVO_4

BiVO_4 was synthesized by the co-precipitation method in presence of urea, followed by annealing process. Typically, 20.0 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 200 mL of HNO_3 (2M) for about 30 min under stirred to give solution A. 20.0 mmol of NH_4VO_3 was dissolved in 200 mL of water to give solution B. The solution B was stirred for about 230 min at 70 °C until a uniform transparent yellow solution. The solution B was drop by drop into solution A, a dark yellow solution was obtained. A certain amount of urea were added to the mixture to obtain the molar ratio of Bi:V: urea = 1:1:3.125. The obtained mixture was vigorously stirred for 30 min then heated at 85 °C (RT) to evaporate the water for overnight. Finally, the obtained powder was calcined at 300, 350, 400 and 450 °C for 3h with a heating rate of 5 °C/min from room temperature to the annealing temperature. The as-calcined sample was denoted as RT, 300 °C, 350 °C, 400 °C and 450 °C.

2.3. Characterization

The phase structures of BiVO_4 were characterized by the powder X-ray diffraction (XRD) patterns on a D8 Advance Bruker powder diffractometer with a $\text{Cu K}\alpha$ excitation source at a scan rate of 0.030 °/s in the 2-theta range of 5-80 °. The morphology of the as-prepared BiVO_4 were visualized by scanning electron microscope (SEM, JEOL JSM 7401F) with an accelerating voltage of 3 kV.

2.4. Photocatalysts Test

Photocatalytic activity of products were prepared experimentally during the decomposition of toxic organic pollutants as Rhodamine B (RhB). In each sample experimental, a 0.1 g amount of photocatalyst was added into 100 mL of RhB solution with a concentrations of 1×10^{-5} M and using a compact Philip lamp (40W, Vietnam) as the visible-light resource. The mixture is stirred with a magnetic stirrer at 550 rpm. Before lighting, the mixture was continuously stirred in the dark for 1 hour to ensure adsorption balance. After, the suspension was exposed to visible light irradiation while being vigorously stirred. The suspension (5 ml) was taken out at 45g min intervals and centrifuged to remove the photocatalyst particles for the analysis of the RhB. The concentration (C) of RhB in the solution after time was monitored using a Thermo Evolution 60S UV-Visible Spectrophotometer. The wavelength were recorded is 554 nm. The C/C_0 ratio was calculated to evaluate the photocatalytic efficiency of the as-prepared m- BiVO_4 samples.

3. Results and Discussion

3.1. XRD analysis

We are investigating the effect of calcined temperatures on the formation of the BiVO_4 crystalline phase and all samples are calcine at different temperatures. Fig. 1 shows the XRD patterns of the BiVO_4 -T sample calcined at 300°C; 350°C, 400°C; 450°C for 5h and RT. No significant characteristic peaks for BiVO_4 because of the sample stirred and heated at 85 °C as show fig 1a. All sample calcined temperatures with characteristic peaks with 2θ at 18.5, 29, 30.6, 35 and 46° and the diffraction peaks could be indexed to the pure monoclinic scheelite BiVO_4 phase (JCPDS card no. 14-00688). The similar XRD patterns of BiVO_4 were also conform according to researchers [25.26].

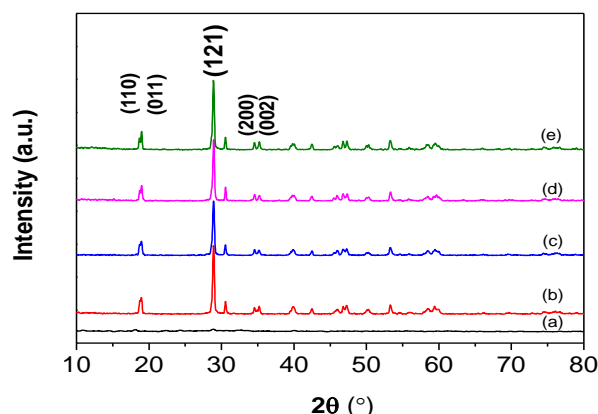


Figure 1. XRD patterns of the different BiVO₄-T samples (a) RT; (B) 30; (C) 350; (D) 400 and 450

3.2. SEM analysis

Fig. 2 shows the SEM images of all sample by the co-precipitation method at calcined temperatures and RT. When the sample was calcined as shown in fig 2(b-e), it shows the structure of the nanoparticles as well as grape-like morphology and the grape of create cluster. However, fig 2a shows the RT sample Form the adhesive sheet together. Because, it has a urea concentration that does not completely burn at 85 °C. According to the above SEM observations, we can thus assume that calcined temperature is a crucial role in determining the crystal structure. Moreover, it can be deduced from the above results that the morphology as well as size of the grape could be easily controlled by varying urea concentration and calcined temperatures time.

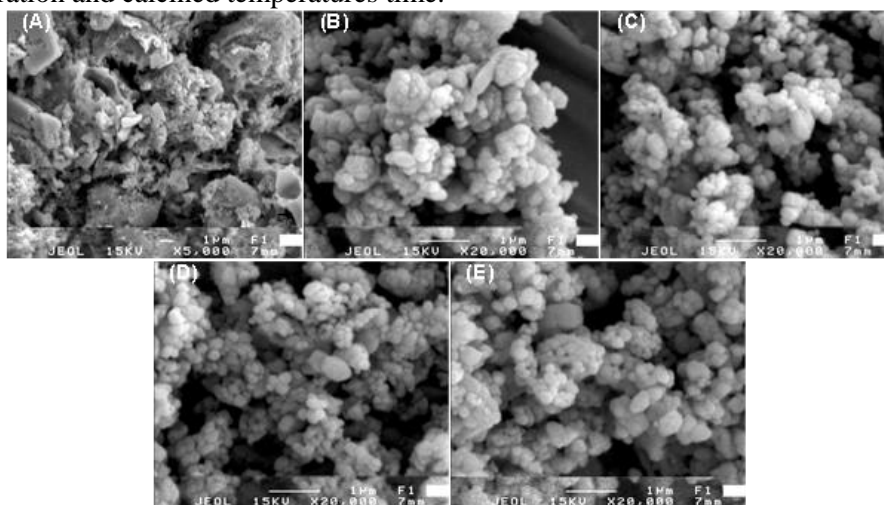


Figure 2. SEM images of (a) RT; (B) 300; (C) 350; (D) 400 and 450

3.3. Photocatalytic activity

We examined photocatalytic degradation of RhB dye solution under visible-light. Fig 3a shows more than 83.4% concentrations degradation of RhB is observed over sample 350 within 270 min under visible-light. The photocatalytic activity on the BiVO₄-T (T is the calcined temperatures) decreases in the following order: BiVO₄-350, BiVO₄-300, BiVO₄-400 and BiVO₄-450, the rate constant (k) as show at table 1. The results of the photocatalytic activity showed that BiVO₄-350 was the best sample at concentrations 1×10^{-5} mol L⁻¹ in RhB.

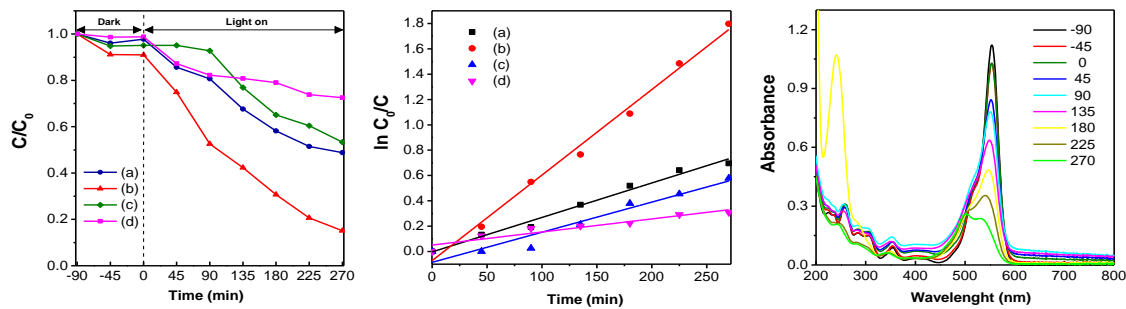


Figure 3. (A) Photocatalytic activity of BiVO₄-T crystallites with different T values: (a) 300; (b) 350; (c) 400; (d) 450, (B) ln(C₀/C) versus time and (C) Absorption changes of RhB aqueous solution in the presence of BiVO₄-350

Table 1. Lattice parameters (Å); Volume (Å³); Crystallite size(nm); the rate constant (K) and Correlation coefficients (R²) of BiVO₄-T

Sample	Lattice parameters (Å) ^a			Volume ^a (Å ³)	Crystallite size ^a (nm)	Kapp ^b (× 10 ⁻³)	R ² ^b
	a	b	c				
300	5.1823	11.6972	5.0973	308.9924	29.47	1.4637	0.9857
350	5.1798	11.6967	5.1037	309.2230	28.13	2.5729	0.9928
400	5.1849	11.69167	5.0923	308.6988	30.33	2.7137	0.9389
450	5.1864	11.6963	5.0882	308.6665	29.64	1.4094	0.9147

^a Data obtained by XRD data; ^b Data obtained by the relationship between ln(C₀/C) and irradiation time t (min)

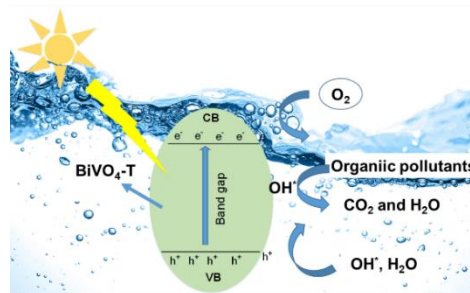
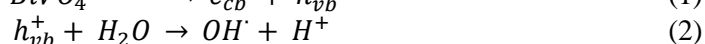
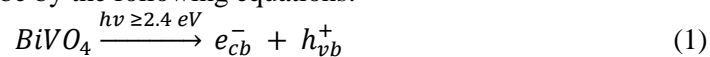


Figure 4. Schematic illustration for Photocatalytic activity of BiVO₄

Fig. 4. Show as The schematic illustration for Photocatalytic activity of BiVO₄. This reaction would be by the following equations:



The scheelite BiVO₄ with a band gap of 2.4 eV and Wavelength respectively is 554 nm (Ep. (1)). Ion OH⁻ can react with h_{vb}⁺ on valency to produce additional OH[·] (Ep. (3)). The other hand whereas, e_{cb}⁻ tend to re-associate with h + vb attached to release heat (t) or light (L) (Ep. (4)). The OH[·] with high oxidation that can decompose compounds Organic with the final product is CO₂, H₂O and Inorganic ions are less toxic.

4. Conclusions

We have successfully synthesized a BiVO₄ photocatalysts via co-precipitation method. The calcined temperature is a crucial role in determining the crystal structure. The result indicates that all samples calcined are monoclinic scheelite structure of BiVO₄. The photocatalytic activity results indicated the BiVO₄-350 sample to have good photocatalytic activity. The degradation efficiencies of RhB achieved

83.4 % after 270 min irradiation. Moreover, the present study motivates us to explore Urea concentration increase and calcined temperature to better results.

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