



# Effects of Cu dopants on the structures and photocatalytic performance of cocoon-like Cu-BiVO<sub>4</sub> prepared via ethylene glycol solvothermal method



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## ABSTRACT

A series of cocoon-like hierarchical structures xCu-BiVO<sub>4</sub> photocatalysts were successfully synthesized by ethylene glycol solvothermal method with ethylene diamine tetraacetic acid (EDTA) as the chelating agent. The as-prepared samples were characterized by XRD, XPS, SEM, BET, UV–Vis DRS and PL, respectively. It was shown that the amount of Cu<sup>2+</sup> has no effect on the crystal phases of BiVO<sub>4</sub> but plays an important role on the morphology, the catalysts turned from flower-like into cocoon-like hierarchical structures due to Cu<sup>2+</sup> doping. Results showed that Cu<sup>2+</sup> doping can effectively enhance the photocatalytic activities of the BiVO<sub>4</sub> which were evaluated by the degradation of Rhodamine B (RhB) under visible-light irradiation. The improvement of photocatalytic activity is due to the changed morphology, the enhancement of light absorption, narrower band gap and lower recombination ratio of photo-induced electron-hole pairs. The best photocatalytic performance is obtained for 1.5Cu-BiVO<sub>4</sub>, of which the Rhodamine B (RhB) photo-degradation rate can reach to be 96% after 50 min under visible-light irradiation. The stable xCu-BiVO<sub>4</sub> will be a promising photocatalytic material applied in degradation of organic pollutants.

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## 1. Introduction

Photocatalytic degradation of organic pollutants has been known as one of the most promising strategies to create the clean and unpolluted environment for human beings in modern society. The success of photocatalytic degradation greatly depends on the suited selection of photocatalyst materials. In this regard, bismuth vanadate (BiVO<sub>4</sub>) has attracted considerable attention due to its high stability, narrow band gap, non-toxicity, and advanced visible-light utilizing capacity [1,2]. BiVO<sub>4</sub> is a typical ternary semiconductor which has a layered structure, and have three crystallographic forms, that is, monoclinic scheelite-like, tetragonal scheelite-like and tetragonal zircon-like, where phase transitions may take place between these phases under different thermal conditions [3]. It was reported that monoclinic BiVO<sub>4</sub> with a 2.4 eV band gap could absorb the solar spectrum up to the

blue light region of approx. 520 nm, resulting in the fact that monoclinic scheelite structured BiVO<sub>4</sub> could exhibit far better visible-light-driven photocatalytic performance over the other crystal forms [4,5].

However, an insufficient charge separation of the photo-excited electron-hole pairs in pure BiVO<sub>4</sub> limited its activity. Since then, many attempts have been made to enhance the photocatalytic efficiency of BiVO<sub>4</sub>, by inducing structural changes by metal ions doping. To date, many metals, such as Fe [6], Co [7], Ag [7–9], Ni [10], Er [11], Gd [12], Cu [13–16], and other metals doped in BiVO<sub>4</sub> have been demonstrated to be effective in the enhancement of their photocatalytic activities. Therefore, BiVO<sub>4</sub> doped with metal ions or metal oxides is considered to be a feasible route for enhancing the photodegradation of organic contaminants.

Therefore, to further enrich various photocatalytic materials with visible light catalytic efficiency, we design and synthesis a cocoon-like Cu-BiVO<sub>4</sub> composite by doping Cu element to BiVO<sub>4</sub>. Although there are some reports about Cu doping BiVO<sub>4</sub> [13–16], to the best of our knowledge, the cocoon-like hierarchical structures Cu-BiVO<sub>4</sub> has been rarely reported. In addition, the same

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metal ion doped the same photocatalyst prepared with different synthesis methods would give rise to different results. Hence, in the present work, we synthesized the  $\text{Cu}^{2+}$  doped  $\text{BiVO}_4$  composite by ethylene glycol solvothermal method with ethylene diamine tetraacetic acid (EDTA) as the chelating agent, which was also rarely reported for the  $\text{Cu}^{2+}$  doped  $\text{BiVO}_4$  photocatalyst. And the structures of  $x\text{Cu-BiVO}_4$  were also characterized by XRD, SEM, BET, XPS, UV–Vis and PL. Rhodamine B (RhB) was chosen as model pollutants to evaluate the photocatalytic performance under visible light irradiation.  $\text{Cu}^{2+}$  doping can suppress the recombination of photogenerated electron-hole pairs, which benefited to the enhancement of photocatalytic activity evidently. Afterwards, the possible photocatalytic mechanism of  $\text{Cu-BiVO}_4$  photocatalyst was also discussed.

## 2. Experiment

### 2.1. Synthesis of $x\text{Cu-BiVO}_4$ photocatalyst

Facile solvent thermal synthesis is shown in the following way: 4.8507 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was dissolved in 50 mL ethylene glycol. The mixture was stirred for 0.5 h at  $80^\circ\text{C}$  and then added 1.1698 g  $\text{NH}_4\text{VO}_3$ . The mixture was stirred continuously until the colour of solution turned to transparent orange-yellow. 3 g EDTA was then added into the mixture and the pH of the mixture was adjusted to approximately 11 using an ammonia solution with vigorous stirring. Then different contents of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  ( $n(\text{Cu}^{2+})/n(\text{Bi}^{3+}) = 0, 0.005, 0.01, 0.015, 0.02, 0.025$ ) were added into these suspensions with continuously magnetic stirring for 30 min, respectively. Afterwards, each precursor was directly transferred into 100 mL Teflon-lined stainless autoclave, respectively, heated by drying cabinet at  $180^\circ\text{C}$  for 10 h. Then the autoclave was cooled at room temperature, vividly yellow precipitates were filtered and washed with absolute ethanol and distilled water for several times, and then dried at  $80^\circ\text{C}$  in the air for 12 h to get  $\text{BiVO}_4$  with different  $\text{Cu}^{2+}$  doping contents. For convenience, the sample was identified as  $x\text{Cu-BiVO}_4$ , where  $x\%$  symbolized the initial molar ratio of Cu to Bi ( $x = 0.5, 1.0, 1.5, 2.0$ , and  $2.5$ , respectively).

### 2.2. Characterization of photocatalysts

The crystal phases of the samples were analyzed using an X-ray diffractometer with  $\text{Cu K}\alpha$  radiation (XRD-D/max RA, Rigaku, Japan). The binding energies of Bi, V, Cu, and O were measured at room temperature using an X-ray photoelectron spectroscope (XPS, VGESCALAB MARK II) using  $\text{Mg K}\alpha$  radiation. SEM images were taken with Hitachi S-3000N field emission scanning electron microscopes. The Brunauer–Emmett–Teller (BET) surface areas were obtained using the nitrogen adsorption–desorption isotherms determined at the temperature of liquid nitrogen on an automatic analyzer (Autosorb-iQ-MP, Quantachrome, USA). Absorption spectrum was carried out by an UV–vis spectrophotometer (TU-1901), using  $\text{BaSO}_4$  as reference. The photoluminescence (PL) spectra were investigated on an F-2700 fluorescence spectrophotometer (Hitachi, Japan) at room temperature.

### 2.3. Evaluation of photocatalytic activity

Visible-light photocatalytic activities of all prepared samples were evaluated through the degradation process of Rhodamine B (RhB) in an aqueous solution. A 250 W halogen lamp light was used as the simulated visible-light source. In all of the photocatalytic experiments, 30 mg of photocatalysts was added into 50 mL Rh B solution with a concentration of 15 mg/L. Before illumination, the suspensions were stirred in dark for 30 min to

ensure the adsorption-desorption equilibrium between RhB and photocatalysts. Afterwards, the suspensions were stirred and exposed to simulated visible-light irradiation. At given time intervals, 5 mL of the suspensions were collected and filtered through a  $0.45\ \mu\text{m}$  millipore filter to remove the photocatalyst particles. The concentrations of RhB solutions were checked by recording the absorbance at 554 nm using an UV-1800 UV–vis spectrophotometer (Puxi, China).

## 3. Results and discussion

### 3.1. Crystal structure analysis

Fig. 1 shows the crystal structure and phase purity of the samples. All the diffraction peaks of as-prepared  $x\text{Cu-BiVO}_4$  correspond to the (011), (121), (040), (200), (211), (051), (042), (202), and (321) planes, which are consistent with the basis of monoclinic  $\text{BiVO}_4$  (JCPDS no.14-0688). The XRD patterns for all  $x\text{Cu-BiVO}_4$  samples present similar and the intensity of peaks is strong and no other impurities such as  $\text{CuO}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Bi}_2\text{O}_3$  or organic compounds related to reactants were detected, suggesting the higher crystallinity and phase purity of  $x\text{Cu-BiVO}_4$  samples. However, the intensity of (–121) peak decreases with an increase of Cu doping content, which revealed that  $\text{Cu}^{2+}$  was doped into the  $\text{BiVO}_4$  lattice and led to a reduction in the crystallization of  $\text{BiVO}_4$ . Furthermore, the peak splitting ((200), (020)) disappeared (Fig. 1) after  $\text{Cu}^{2+}$  doped, which meant that  $\text{Cu}^{2+}$  doping inhibited the growth of (200) and (020) planes.

The average crystallite sizes of all samples were calculated according to the line width analysis of the (121) diffraction peak based on Scherrer equation [17] and the results are listed in Table 1. To further analyse the effect of Cu doping on the crystal structure of  $\text{BiVO}_4$ , the lattice parameters of the samples were calculated using Bragg's law ( $2d\sin\theta = \lambda$ ) and the formula ( $(1/d^2) = (h^2 + k^2/a^2) + (l^2/c^2)$ ), which is applicable to monoclinic systems, and the results are summarized in Table 1. As shown in Table 1, the crystallite sizes and the lattice parameters of the  $x\text{Cu-BiVO}_4$  samples decrease with increasing doping content, it can be deduced that  $\text{Cu}^{2+}$  doping may result in a slight lattice distortion in the structure of  $\text{BiVO}_4$ .

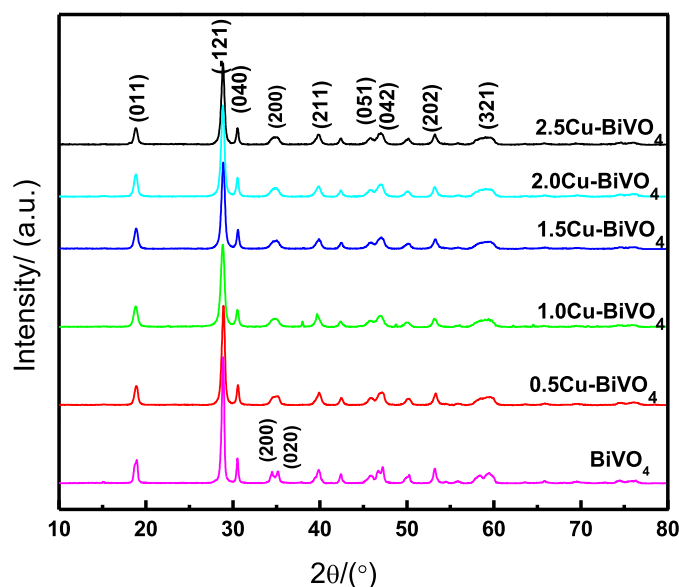


Fig. 1. XRD patterns of  $x\text{Cu-BiVO}_4$  samples with various Cu doping contents ( $x = 0, 0.5, 1.0, 1.5, 2.0, 2.5$ ).

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