Fabrication of Co$^{3+}$ and B co-doping BiVO$_4$ with improved photocatalytic performance for organic degradation

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Abstract. Co$^{3+}$ and B co-doping BiVO$_4$ photocatalysts were successfully prepared for organic pollutants degradation through sol-gel and impregnation two-step process. Their structure, surface chemical composition, and optical absorption were characterized. All as-prepared samples consisted of the monoclinic phase. It was found that the Co dopants existed in the form of CoO$_x$ in B-BiVO$_4$, thus a p-n heterojunction formed in BiVO$_4$. The optical absorption results reveal that CoO$_x$ could greatly enhance the absorption and decrease in the band-gap energy of BiVO$_4$. The 0.5% Co$^{3+}$ doping B-BiVO$_4$ sample exhibited the highest photocatalytic activity for methyl orange photocatalytic degradation, being approximately 92% of MO degradation rate under 50 min visible light irradiation.

1 Introduction

As one of the non-titania visible-light-driven photocatalysts, BiVO$_4$ has recently attracted considerable attention, as it is commonly used as a photocatalyst in water splitting and oxidative decomposition of organic pollutants under visible light irradiation [1-5]. It has been found that the photocatalytic activity of BiVO$_4$ is determined by its crystal phase. BiVO$_4$ with a monoclinic scheelite structure can show photocatalytic properties and is commonly used as a photocatalyst in water splitting and oxidative decomposition of organic contaminants under visible light irradiation [6-8]. The photocatalytic activity of pure BiVO$_4$ still needs improvement due to its high rate of photogenerated electron-hole pair recombination. The introduction of dopant elements causes the formation of charge traps for electrons and/or holes and thus prolongs the recombination time [9].

In the current study, the strategy of Co$^{3+}$ and B co-doping was employed to improve the photocatalytic performance of BiVO$_4$ photocatalyst. The Co$^{3+}$ doping B-BiVO$_4$ photocatalysts were successfully prepared for organic pollutants degradation through sol-gel and impregnation two-step process. The effects of Co$^{3+}$ doping on the structure, light absorption ability and photocatalytic performance of B-BiVO$_4$ were studied in detail.

2 EXPERIMENT

2.1 Photocatalyst preparation

The BiVO$_4$ and B-BiVO$_4$ precursors were synthesized through a sol-gel method as reported in reference [10]. The Co$^{3+}$ and B co-doping BiVO$_4$ samples were prepared by the impregnation method. The B-BiVO$_4$ precursor powder (3.0 g) was added to 2 mL of distilled water containing an appropriate amount of Co(NO$_3$)$_3$ in a ceramic dish. Water was evaporated at 353 K. The suspension was stirred using a glass rod during evaporation. The resulting powder was collected and calcined in air at 500 °C for 5 h, and then cooled to room temperature to obtain Co$^{3+}$ doping B-BiVO$_4$ samples, labeled as xCo-B-BiVO$_4$ nanoparticles. The Co doping concentration (x wt %) was chosen as 0.3, 0.4, 0.5, 0.6, and 0.7, which is the weight percentage of Co(NO$_3$)$_3$ to BiVO$_4$. 0.5Co doping BiVO$_4$ was prepared with the same impregnation method except that its precursor is pure BiVO$_4$. For comparison, pure BiVO$_4$ and B-BiVO$_4$ were prepared according to reference [10].

2.2 Characterization of photocatalyst

The X-ray diffraction (XRD) spectra of the catalysts were obtained by X-ray diffraction (XRD) with Cu K$\alpha$ radiation (model D/max RA, Rigaku, Japan). The accelerating voltage and the current were 40 kV and 150 mA, respectively. The morphologies of the samples were observed with a field emission scanning electron microscope (SEM, S-3000N, Hitachi, Japan), and the chemical composition of the photocatalysts was determined using an energy dispersive X-ray spectrometer (EDS) attached to the SEM. The binding energies of Bi, V, Co, B, and O were measured at room temperature using an X-ray photoelectron spectroscopy (XPS, VGESCALAB MARK II) using Mg K$\alpha$ radiation. The diffuse reflectance spectra (DRS) were obtained for...
the dry-pressed disk samples using a UV-vis spectrophotometer (TU-1901, Puxi, China) equipped with an integrating sphere assembly using BaSO₄ as the reflectance standard. The spectra were recorded in the wavelength range from 230 to 800 nm at 25 ± 1 °C.

2.3 Photocatalytic performance test

The photocatalytic activities of the samples were determined by measuring the degradation of methyl orange (MO) in an aqueous solution under visible light irradiation. In the activity test, a 250 W tungsten halogen lamp with a < 420 nm cutoff filter was used as visible light source. The photo-degradation experiment was performed according to the following process: The photocatalyst (0.01 g) was suspended in 50 mL aqueous solution of methyl orange with the initial concentration of 15 mg/L. The suspension was vigorously stirred with a magnetic stirrer in the dark for 60 minutes prior to illumination to achieve adsorption/desorption equilibrium, as well as in the photoreactor throughout the experiment. At given time intervals, the collected samples were filtered through a 0.45 μm Millipore filter to remove catalyst particles. The filtrate concentration was monitored by recording the absorbance at 464 nm, the maximum absorption wavelength for methyl orange, using a UV-1800 UV-Vis spectrophotometer (Puxi, China).

3 Results and discussion

3.1 XRD analysis

The XRD patterns of as-prepared samples are shown in Fig. 1. All the as-prepared samples exhibited typical peaks of monoclinic BiVO₄ (JCPDS cards No. 75-1866)[2,5]. Although some studies in the literature have reported that Co(NO₃)₂ can be transformed into Co₃O₄ during the calcination process [11], no Co₃O₄ peaks were found in XRD analysis, which might be attributed to the low Co content. Fig. 1 (B) shows the shift of the peaks at approximately 28.8 and 30.5° corresponding to the (121) and (040) planes, respectively. The peaks shift toward the left in the case of B single doping, but our results show a gradual shift toward the right as the Co doping content increased. The right shift suggests that the Co cation was successfully doped into the BiVO₄ and the increased amount of Co dopant in the samples lead to a change in the local crystal structures by a few degrees.

3.2 SEM analysis

The morphology of the synthesized samples was analyzed by SEM. Fig. 2 shows the three typical SEM images of the BiVO₄, B-BiVO₄, and B-0.5Co-BiVO₄ photocatalysts. All three samples displayed a sphere-like morphology, but there is a minor difference in the morphologies and particle shapes of the samples between pure BiVO₄ and B-BiVO₄. After Co doping, the sizes of some particles decreased, which could cause an increase in the surface area of the sample. The composition of the B-0.5Co-BiVO₄ sample is determined by energy dispersive X-ray spectroscopy (EDX) experiments. As shown in Fig. 2d, we can see the clear signals for Bi, V, O, and Co.

3.3 XPS analysis

The chemical states and chemical compositions of the samples are investigated through XPS. Fig. 3 shows the Co 2p (a), Bi 4f (b), B 1s(c,d), V2p(e), and O1s(f) XPS spectra of the as-prepared samples. The Co 2p high-resolution XPS scan spectrum is shown in Fig. 3 (a). Two peaks at 780.7 and 797.3 eV, which can be assigned to the Co 2p3/2 and Co 2p1/2, respectively, were observed. These peaks are very close to those of Co₃O₄ [12], for which corresponding peaks were reported at 780.8 and 797.1 eV.

Fig. 3(b) shows the Bi 4f high-resolution XPS scan spectrum of pure BiVO₄, B-BiVO₄ and 0.3 B-0.5Co-BiVO₄; the binding energies of Bi 4f appear at 159.1~159.5 eV and 164.4~165.2 eV for Bi 4f1/2 and Bi 4f3/2, respectively, which are characteristic of the Bi²⁺ species [2-7]. The B 1s XPS spectra of the B-doped and B-Co codoped samples are shown in Fig. 3(c) and (d). Each XPS spectrum of B 1s in Fig. 3(c) and (d) exhibits an asymmetric broad peak from 184 to 191 eV, which is a typical characteristic peak for B 1s species. The asymmetric peak was deconvolwed into two components at E₀ = 184.2 and 190.8 eV for B-BiVO₄ and...


\[ E_0 = 184.3 \text{ and } 188.8 \text{ eV for B-0.5Co-BiVO}_4. \]  

The peak at 184.2 and 185.5 eV is assigned to Bi,C [13], which showed no photocatalytic activity.

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Energy chemical binding of which correspond the V for BiVO._4_ approximately 7 eV for pure BiVO._4_. The standard binding energies for B1s in B with direct transition at 1.45 and 2.07 eV [12], corresponding, respectively, to edges of O²⁻→Co³⁺ excitation and O²⁻→Co²⁺ charge transfer. The latter is the basic optical band gap energy for interband transitions. CoO₄ has absorption in nearly the entire visible range of the spectrum and induces an extension of the light absorption spectrum of the composite semiconductor even with low cobalt content. Thus, with the increase of Co doping concentration, the absorption is strengthened in the visible region, and the band gap energies decrease.

The band gaps of Co-doped and xCo-BiVO₄(x is 0.3, 0.4, 0.5, 0.6, 0.7) are 2.33, 2.31, 2.26, 2.23, 2.21 and 2.11, respectively.

**3.5 Photocatalytic performance**

The photocatalytic degradation of MO dye on the as
prepared BiVO₄ catalysts was carried out under visible-light irradiation. The results are shown in Fig. 5. It shows that only a small amount of MO could be degraded through either direct photolysis in the absence of catalyst or adsorption in the dark. The evidence indicates that the pure BiVO₄ catalysts exhibited low visible light photocatalytic efficiency for the degradation of MO within 50 min irradiation. Compared with pure BiVO₄, B- and Co- single doped BiVO₄ can enhance the photocatalytic activity to some degree. However, it can be observed that B-Co co-doping can increase BiVO₄ photocatalytic activity effectively. The MO photocatalytic degradation rate for B-Co co-codoped BiVO₄ increases with Co doping content when the doping Co is lower than 0.5%, but decreases when the amount of Co is higher than 0.5%. The degradation rate of MO can be up to 92% in 50 min. So the optimal mole percentage of Co doping in B-Co codoping BiVO₄ is 0.5%. These results confirmed that Co and B elements exhibited a synergetic effect on the improvement of photocatalytic activity efficiency. Moreover, as displayed in Fig. 5(B), the photocatalytic degradation of MO solution fitted well with the pre-first-order kinetics fitted well with the Langmuir-Hinshelwood (L-H) model within 50 min.

Fig. 5 (A) MO degradation under visible light illumination for 50 min in the presence of B-BiVO₄ with various nickel doping, pure BiVO₄ and without photocatalyst; (B) $ln(C_t/C_0)$ versus time for B-BiVO₄ doping concentrations of a. BiVO₄, b. B-BiVO₄, c. 0.5Co-BiVO₄, d. 0.3Co-BiVO₄, e. 0.4Co-BiVO₄, f. B-0.5Co-BiVO₄, g. B-0.6Co-BiVO₄, h. B-0.7Co-BiVO₄.

Based on the above analysis, the scheme that the as prepared Co³⁺ and B codoped BiVO₄ catalysts exhibited higher photocatalytic efficiency can be explained as following scheme (Fig. 6): in the case of Co³⁺ and B codoped BiVO₄, on the one hand, the impurity energy levels are introduced above the valence band due to B dopants, thus causing the absorption edge to shift into the visible region. The impurity levels create another possible transition route for excited electrons during visible light irradiation, which electrons are promoted from the Bi¹ˢ level to the conduction band of BiVO₄. On the other hand, because the CoO₂ [23] is a p-type semiconductor and BiVO₄ is an n-type material [1], a p-n heterojunction formed at the interface of the two materials in the composite photocatalysts. The photoinduced electrons on the BiVO₄ particle surface can easily migrate to CoO₂ via interfaces; similarly, photoinduced holes on the CoO₂ surface can transfer to BiVO₄ owing to the different valence band edge potentials. As a result, a larger amount of electrons on the CoO₂ surface and holes on the BiVO₄ surface can participate in photocatalytic reactions to directly or indirectly decompose MO, thus enhancing the photocatalysis efficiency.

However, more CoO₂ can also act as recombination centers for the electrons and holes. Therefore, an appropriate amount of the doped Co in B-BiVO₄ catalysts is necessary so that the recombination of photogenerated electrons and holes can be suppressed effectively. It is interesting to note that the photocatalytic activities of B and CoO₂ codoped BiVO₄ catalysts enhance with the increase in Co doping content up to 0.5% and then decrease. A similar result was also reported by Zhang et al. [30]. It is hypothesized that high CoO₂ content is harmful to the photocatalytic activity because of the excess coverage of active sites on the BiVO₄ surface by CoO₂ particles and can also act as recombination centers for the electrons and holes [16].

Fig. 6 Proposed degradation scheme of organic pollutants by B-Co-BiVO₄ under visible light irradiation.

4 Conclusions

Co³⁺ and B codoped BiVO₄ catalysts were successfully prepared through a sol-gel and impregnation two-step process. Compared with the pure BiVO₄, B-, Co- single-doped BiVO₄, the Co³⁺ and B codoped BiVO₄ exhibits higher photoactivity under visible light. These samples show higher photocatalytic activity for methyl orange photocatalytic degradation, and the highest degradation rate for B-0.5Co-BiVO₄ can reach to be approximately 92% under visible light irradiation in 50 min. The B dopants led to impurity energy levels above the valence band and a p-n heterojunction formed due to CoO₂ being a p-type semiconductor and BiVO₄ an n-type. Codoping can narrow the band gap. The synergetic effects of B and CoO₂ may efficiently promote the separation of photogenerated holes and electrons and are the main reasons for the high photodegradation rate of dye pollutants under visible light irradiation.

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