Synthesis, characterization, and photocatalytic activities of Eu³⁺-doped BiVO₄ catalysts

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An improved sol-gel technique was utilized to synthesize the Eu^{3+} -doped bismuth vanadate (BiVO₄) photocatalysts, resulting in enhanced photocatalytic activity. The photocatalytic properties and structural composition of the catalyst were rigorously examined by XRD, SEM, EDS, XPS, and DRS. The XRD analysis confirmed the successful incorporation of Eu^{3+} into the host lattice of BiVO₄. The photocatalytic efficiency of the BiVO₄, with the 7% Eu^{3+} -doped BiVO₄ sample exhibiting the highest photocatalytic activity. The boosting of photocatalytic efficiency can be caused by the additional oxygen vacancies, narrower band gap, and decreased rate of photoexcited electron-hole pair recombination caused by Eu^{3+} doping.

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1. Introduction

The increasingly serious water pollution caused by industrial production poses serious threats to environmental security and the health of the human. Photocatalytic oxidation has been widely acknowledged as an efficacious approach for the decomposition of toxic and environmentally hazardous organic pollutants in water. Titanium dioxide (TiO₂), a widely used photocatalyst, has demonstrated strong catalytic activity in wastewater treatment and the degradation of organic compounds under UV exposure [1, 2]. However, its wide bandgap, rapid recombination process of photoexcited electron-hole pairs, and low quantum yield of hydroxyl radicals limit its effectiveness as a photocatalyst. Therefore, there is an urgent need for the development of highly active, stable, and novel photocatalysts that can be activated by visible light [3-5].

Bismuth vanadate (BiVO₄) with a scheelite structure has shown excellent photocatalytic activity against organic compounds under visible light [6, 7]. However, like TiO₂, pure BiVO₄ suffers from similar problems such as rapid recombination of electron-hole pairs. Recent studies have indicated that ion doping, particularly with transition metals, offers a convenient and cost-effective approach to enhancing the efficiency of photocatalysts by improving stability and

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activity. To enhance the photocatalytic efficiency of BiVO₄, a range of noble metal and transitionmetal composites have been incorporated to augment the properties of the pure BiVO₄, such as BiVO₄/NiFe₂O₄, Pt-Cu₂O-BiVO₄, Ni/BiVO₄, Zn/BiVO₄, Ce/BiVO₄, and Gd/BiVO₄ [8-13].

In this study, Eu³⁺-doped BiVO₄ was synthesized using an improved sol-gel method. Methylene blue (MB) as a simulated pollutant for visible-light degradation was utilized to assess the photocatalytic activity of the tested particles. The Eu³⁺-doped BiVO₄ photocatalysts were comprehensively characterized using X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy, and diffuse reflectance spectroscopy. Additionally, the relationship between the photocatalytic efficiency and structural composition of the samples was also assessed.

2. Experimental

2.1. Synthesis of materials

A stoichiometric mixture of ammonium metavanadate (NH₄VO₃) and citric acid (CA) was dissolved in ammonia water, followed by thorough stirring until a pale yellow solution, labeled as solution A. A certain molar amount of bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), europium nitrate pentahydrate (Eu(NO₃)₃·5H₂O), and CA were dissolved in nitric acid (HNO3) with continuous stirring for approximately 30 minutes, resulting in a clear solution labeled as solution B. Upon combining solution B with solution A, a homogenous dark green solution, denoted as solution C, was obtained. To prepare solution D, ethylenediaminetetraacetic acid (EDTA) dissolved in ammonia water was added into solution C. Then, a stoichiometric quantity of solid EDTA was introduced resulting in a pale blue solution. The prepared solution D was mixed for 45 min, followed by heating to 80 °C to facilitate the evaporation of water. The resultant gel was subsequently calcined in an oxygen-rich environment at 450 °C for 3 h, producing Eu³⁺-doped BiVO₄ powders with different concentrations of Eu³⁺ (0, 0.01, 0.03, 0.05, 0.07, and 0.10). These samples are labeled as Eu00, Eu001, Eu003, Eu005, Eu007, and Eu010 for subsequent reference.

2.2. Characterization

The crystalline properties of the photocatalysts were assessed using an XRD (model DX-2000, Rigaku, Japan). The analysis was conducted with Cu $K\alpha$ radiation at a wavelength of 1.5408 Å, across a scanning range from 10° to 80°, with a step increment of 0.02°. The size and morphology of the photocatalysts were examined through a SEM and an EDS (model SU8010, Hitachi, Japan). The surface structures were characterized by the XPS (model Nexsa G2, Thermo Scientific, USA). The DRS was obtained by ultraviolet-visible diffuse reflectance spectroscopy (model V-6500, Jasco, Japan).

2.3. Photocatalytic activity

A total of 0.15 g photocatalyst powders were dispersed into 100 mL solution of MB $(4.2 \times 10^{-5} \text{ mol/L})$. First, the reaction blending was vigorously mixed with a magnetic stirrer for one hour in the absence of light to achieve the equilibrium of the powders and MB. Thereafter,

the suspension was subjected to illumination by the 300 W Xe lamp. At regular time intervals, samples were taken from the suspension, and the photocatalyst powders was separated through centrifugation before measuring the MB concentration in the supernatant via spectrophotometry. The efficiency of MB photodegradation was assessed using the following mathematical equation:

$$\eta = \frac{C}{C_0} \tag{1}$$

where C and C_0 denote the post-irradiation and initial absorbance of the MB solution, respectively.

3. Results and discussion

3.1. XRD analysis

Figure1 presents the XRD patterns of Eu^{3+} -doped BiVO₄ photocatalysts. It is observed that all Eu^{3+} -doped BiVO₄ catalysts exhibit the monoclinic scheelite phase (JCPDS, 83-1699), without any additional crystal phases observed. The diffraction patterns observed in Figure 1 align with the crystallographic planes (101), (112), (004), (200), (020), (211), (015), (213), (204), (024), (220), (116), (312), and (206). The XRD analysis confirms the successful integration of Eu^{3+} into the BiVO₄ host lattice, without altering the lattice structure of BiVO₄ during the crystallization process [14, 15].



*Fig. 1. XRD patterns for all Eu*³⁺*-doped BiVO*₄ *samples.*

3.2. SEM analysis

Figure 2 shows the morphologies of the Eu00, Eu003, Eu007, and Eu010 photocatalysts. A consistent reticular sheet-like architecture with an average grain size ranging from 100 to 500 nanometers was measured for all samples, demonstrating remarkable dimensional uniformity. In Figure 2(a), Eu00 exhibits a reticular sheet-like shape with particle sizes ranging from 150 - 250

nm, as previously reported in our study [16]. However, as depicted in Figures 2(b-d), an increase in the concentration of Eu^{3+} does not improve the reticular architecture. In fact, higher Eu^{3+} content leads to a disruption of the reticular sheet-like architecture. An in-depth structural examination using the EDS was performed on the Eu00 and Eu003 samples, as shown in Figure 3. The study reveals that Eu, Bi, V, and O elements are evenly distributed within the designated area [17].



Fig. 2. SEM for Eu00 (a), Eu003(b), Eu007 (c), and Eu010 (d) samples.



Fig. 3. EDS for Eu00(a) and Eu003(b) samples.

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3.3. XPS analysis

The surface characterization employed XPS to ascertain the oxidation states and elemental composition of Eu³⁺-doped BiVO₄. Figure 4 shows the XPS spectra of Eu00 and Eu005, revealing the presence of bismuth (Bi), carbon (C), vanadium (V), oxygen (O), and europium (Eu) elements. The corresponding binding energies for Bi 4f, C 1s, V 2p, and O 1s were measured at about 158.9, 284.8, 517.5, and 530.1 eV, respectively [18, 19]. The detected binding energy peak for the C 1s orbital, observed at 284.8 eV, comes from carbon contamination on the instrument. In the Eu005 sample, an inconspicuous peak of Eu was detected at approximately 1142.3 eV, as depicted in Figure 4(a). Figure 4(b) presents the high-resolution XPS spectrum of Eu005, providing further insight into the valence states of Eu. Eu $3d_{5/2}$ and Eu 3d_{3/2} exhibit unimodal peaks at 1134.7 eV and 1164.5 eV, respectively, indicating that Eu element exists in a trivalent state, denoted as Eu³⁺ [20]. As for the O 1s XPS spectra, illustrated in Figure 4(c, d), reveals an asymmetric peak of approximately 530 eV, which splits into two components: 530.56 and 530.28 eV for Eu00, and 530.36 and 529.9 eV for Eu005. These peaks correspond to lattice oxygen (O_{latt}) and surface adsorbed oxygen (O_{ads}) components. These results indicate an increase in surface oxygen vacancies following Eu³⁺ doping, suggesting the successful incorporation of Eu³⁺ into the BiVO₄ lattice. Furthermore, additional oxygen vacancies in BiVO₄ act as active sites, significantly enhancing its photocatalytic efficiency [21, 22].



Fig.4. Survery (a), Eu 3d (b), and O1s (c, d) XPS spectra for Eu00 and Eu005 samples.

3.4. Optical properties

Figure 5 illustrates the DRS of the synthesized photocatalysts. All samples demonstrate distinctive spectral absorption characteristic within the visible light spectrum. The sharp spectral edges indicate that the observed light absorption stems from fundamental band gap phenomena rather than impurity-induced transitions. In addition, the incorporation of Eu^{3+} results in minor shifts. The blue shifts in optical properties upon Eu^{3+} doping due to a charge transfer phenomenon, specifically involving the f-electrons of Eu^{3+} and the conduction or valence bands of BiVO₄ [23, 24]. To determine the band gap energies (Eg) of photocatalysts, diffuse reflectance spectral data was analyzed, utilizing a mathematical equation as follows:

$$\alpha h \upsilon = A (h \upsilon - E_{\sigma})^{1/2} \tag{2}$$

where A is the proportionality constant, α is the absorption coefficient, and υ is light frequency [25].



Fig. 5. Diffuse-reflectance spectrum for all Eu^{3+} *-doped* $BiVO_4$ *samples.*

The E_g of Eu³⁺-doped BiVO₄ samples can be approximated from the plot of $(\alpha h \upsilon)^2 vs$.

(hv). Analysis of figure 6 reveals that the E_g for different samples is 2.43, 2.42, 2.41, 2.41, 2.38, and 2.40 eV for Eu00, Eu001, Eu003, Eu005, Eu007, and Eu010, respectively. The observed values are lower than those previously reported in the literature [26].



Fig.6. Plots of $(\alpha hv)^2$ vs. (hv) for all Eu^{3+} -doped BiVO₄ samples

3.5. Photocatalytic properties

Figure 7 depicts the change in MB concentration (C/C_0) in relation to exposure time under the influence of photocatalysts with varying concentrations of Eu³⁺ dopant. Pure BiVO₄ achieves a photo-degradation rate of 94.1% after 65 min of irradiation. Under identical conditions, the photo-degradation rates of MB for Eu001, Eu003, Eu005, Eu007, and Eu010 are 96.3%, 98.0%, 98.9%, 99.8%, and 97.7%, respectively. As the Eu³⁺ concentration increases from 0 to 10%, a gradual enhancement in photocatalytic activity is observed peaking at 7% doping before declining. It has been reported that for optimal electron-hole separation in a space charge region, the potential value must exceed a minimum threshold [27-29]. Increasing Eu³⁺ doping raises the surface barrier, and reduces the breadth of the space charge zone, thus facilitating more effective isolation of electron-hole pairs. However, when the Eu^{3+} doping is further increased, the boundary of the charge region significantly narrows, promoting enhanced recombination of electron-hole pairs within the catalyst. The most efficient photocatalytic degradation of MB is achieved with the 7% Eu^{3+} -doped BiVO₄.

The kinetics of the MB photo-degradation reaction were also investigated using the equation as follows:

$$\ln(C_0 / C) = kt \tag{3}$$

where *k* denotes the degradation rate constant, and *t* denotes the irradiation time (in minute).



Fig. 7. The degradation rates of MB under visible-light irradiation for all Eu^{3+} -doped BiVO₄ samples.

Figure 8 shows that the correlation between $\ln(C_0/C)$ and t for all Eu³⁺-doped BiVO₄ exhibits a good linear relationship, indicating that the degradation reactions follow first-order reaction kinetics [30]. The experiment confirmed that the degradation rate constant k of BiVO₄ doped with 7% Eu³⁺ is 0.10106 min⁻¹, showcasing a remarkable increase in efficiency. This rate is 2.49 times greater than that of Eu00, highlighting the significant photocatalytic enhancement achieved through the strategic incorporation of Eu³⁺ ions.



Fig. 8. The correlation between $ln(C_0/C)$ and t (min) for all Eu^{3+} -doped BiVO₄ samples.

4. Conclusions

Monoclinic scheelite Eu^{3+} -doped BiVO₄ photocatalysts with excellent photocatalytic activity were prepared using an improved sol-gel method. XRD, EDS, and XPS analyses confirmed the successful incorporation of Eu^{3+} into BiVO₄. The DRS results showed a reduction in E_g from 2.43 to 2.38 eV with Eu^{3+} doping, indicating the formation of new low-energy level transitions within the band gap. The photo-degradation efficiency of the photocatalysts was investigated by examining the degradation of MB under visible light. Eu^{3+} doping significantly improved photocatalytic efficiency, with the 7% Eu^{3+} -doped BiVO₄ achieving a decolorization rate of 99.8% within 65 min. This improvement was caused by the additional surface oxygen vacancies. The introduction of intermediate energy levels results in a reduced band gap, which decreases the rate of photo-induced electron and hole recombination, thereby enhancing the carrier lifetime. This study presents a straightforward method for creating efficient, visible-light-driven BiVO₄-based photocatalysts aimed at environmentally friendly applications.

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