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# The upconversion and enhanced visible light photocatalytic activity of Er<sup>3+</sup>-doped

# tetragonal BiVO<sub>4</sub>

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Abstract:  $Er^{3+}$ -doped BiVO<sub>4</sub> with tetragonal structure is prepared by the microwave hydrothermal method. X-ray diffraction and Rietveld refinement demonstrate that the structure is transformed from the monoclinic (C2/c:c3) phase to the tetragonal (I41/amd:2) phase by doping  $Er^{3+}$  ions.  $Er^{3+}$  doping also influences the morphology change of BiVO<sub>4</sub> from irregular flake-like crystal to rod-like crystal, which leads to the increase of the surface areas from 3.25 to 11.96 m<sup>2</sup>/g. Compared with the monoclinic BiVO<sub>4</sub>, the upconversion of the  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> occurs through the transitions from the <sup>4</sup>I<sub>15/2</sub> ground state to <sup>4</sup>F<sub>7/2</sub>, <sup>2</sup>H<sub>11/2</sub>, and <sup>4</sup>F<sub>9/2</sub> states, respectively. The photocatalytic experiment indicates that the tetragonal BiVO<sub>4</sub> (8at.%) with a larger specific surface area (9.88 m<sup>2</sup>/g) shows the best photocatalytic activity under visible light irradiation, which can efficiently improve the degradation rate of RhB up to 97.2% at 150min.

Keywords: Semiconductors; BiVO<sub>4</sub>; Er<sup>3+</sup>; Upconversion; Photocatalytic activity

# 1. Introduction

Semiconductor photocatalysts are widely used in the degradation of organic contaminants in wastewater [1-3]. According to the early reports, the monoclinic  $BiVO_4$ 

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(m-BiVO<sub>4</sub>) is the best visible-light-driven photocatalyst, while the photocatalytic activity under visible light irradiation of tetragonal BiVO<sub>4</sub> (t-BiVO<sub>4</sub>) is negligible [4, 5]. Therefore the monoclinic BiVO<sub>4</sub> has been extensively studied as a promising photocatalyst for organic photocatalytic degradation with its narrow band gap (2.4eV) [6, 7]. However, the rapid recombination rate of electron-hole pairs is always the main drawback for monoclinic BiVO<sub>4</sub> to be applied. To solve this problem, different methods have been used to improve the photocatalytic activity of the monoclinic BiVO<sub>4</sub>, such as co-catalysts loading, impurity doping, and the formation of heterojunction [8, 9]. Recently, S. Usai and Sergio Obregón reported that  $Y^{3+}$  or  $Er^{3+}$  doping could induce the monoclinic-tetragonal heterostructure and improve the photocatalytic performance under sun-like excitation [10, 11]. On this basis, we obtained the tetragonal BiVO<sub>4</sub> after doping  $Er^{3+}$  ions. This phenomenon is quite different from the previous reports. In this work, the  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> system exhibits higher photocatalytic activity than that of monoclinic BiVO<sub>4</sub> for the degradation of RhB under visible light irradiation.

#### 2. Experimental

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All the reagents were of analytical grade and were used without any further purification. In a typical preparation process, 0.01mol Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was dissolved in 25mL deionized water and stirred for 20min at room temperature. A quantity of 0.01mol NH<sub>4</sub>VO<sub>3</sub> was dissolved in 25mL 100°C deionized water and stirred for 20min until the dissolution was complete. Then the NH<sub>4</sub>VO<sub>3</sub> solution was added into the Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O solution with magnetically stirring for 20 min, thus forming the jacinth slurry A. The pH of the slurry A was adjusted to 8.5 by adding concentrated NaOH (5mol/L). After stirred

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for several minites, the appropriate contents of  $Er(NO_3)_3 \cdot 6H_2O$  were added to slurry A until the molar ratio of  $n_{Er}$  to  $n_{Bi}$  was 0at.%-12at.%, generating precursors B. Then each precursor was transferred into the polytetrafluoroethylene (PTFE) autoclave (the filling density was 60%) and heated under microwave irradiation using a microwave hydrothermal reactor (Model MDS-8, Sineo, ShangHai). The specific program was as follow. Firstly, the microwave hydrothermal reaction power was set to 300W and the temperature was from room temperature up to 100°C for 6min. Secondly, the microwave hydrothermal reaction temperature was from 100°C to 150°C for 6min and from 150°C to 200°C for 40min, and then it was allowed to cool to room temperature naturally. Finally, the obtained precipitates were washed three times with deionized water and absolute ethyl alcohol, and then dried at 80°C for 12h in air.

The structural properties of the as-prepared samples were determined by an X-ray diffractometer (XRD, D/Max-2200, Rigaku, Japan) with Cu K $\alpha$  radiation ( $\lambda$ =0.15406nm). The morphology was analyzed by using a scanning electron microscope (SEM, S-4800, Hitachi, Japan). The microstructures were investigated by a transmission electron microscopy (TEM) and a high resolution transmission electron microscopy (HRTEM, J EM-2100, Japan). The specific surface area was measured by a specific surface area analyzer (3H-2000BET-A, BJ, China). The adsorbate was N<sub>2</sub> while the carrier gas was He. The UV-vis diffuse reflection spectra were recorded on a UV-vis spectrophotometer (Hitachi U-3900H, Japan), using BaSO<sub>4</sub> as a reference. The upconversion fluorescence spectra were measured using YAG:Nd<sup>3+</sup> (Quanta Ray Lab-170) pulse laser and Ti sapphire sapphire femtosecond laser (Mira-900) as excitation sources, and the output

wavelength was 980 nm. The collection and detection of luminescence were carried out on a spectrometer (SP2750i) with a spectral resolution of 0.008nm. All of the measurements were performed at room temperature. The Zeta potential was identified by Nano Particle and Zeta potential analyzer (Malvern Nano-ZS, UK).

In a process, a 500W xenon lamp was used as a visible-light source. 0.05g photocatalyst was dispersed in 50mL RhB solution (5mg/L) under ultrasonic treatment. Prior to the irradiation, the solution was magnetically stirred in the dark for 30min to achieve the adsorption-desorption equilibrium. The concentration of RhB was determined by recording the absorbance at 553 nm using a UV-Vis spectrophotometer (Model SP-756p).



#### 3. Results and discussion

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Fig. 1(a) shows the XRD patterns of pure BiVO<sub>4</sub> and  $Er^{3+}$ -doped BiVO<sub>4</sub> photocatalysts. It is worth noting that the monoclinic BiVO<sub>4</sub> (JCPDS NO.14-0688) was changed into the tetragonal BiVO<sub>4</sub> (JCPDS NO.14-0133) when  $Er^{3+}$  is incorporated. The observed evolution of the crystalline structure of  $Er^{3+}$ -doped BiVO<sub>4</sub> is significantly different from that previously reported [11], that is merely the tetragonal phase is present when  $Er^{3+}$  content is above 4at.%. In other words,  $Er^{3+}$ -doped BiVO<sub>4</sub> is considered to stabilize the tetragonal structure. In addition, the intensities of the (101) and (200) peaks of the tetragonal BiVO<sub>4</sub> are reduced gradually so that the crystallinity of the composite is decreased.

The Zeta potential of the precursor slurry is 41.20 with the  $Er^{3+}$ -doped BiVO<sub>4</sub> (0at.%) in Fig. 1(c), suggesting the larger electrostatic repulsion, which is responsible for the shortage of BiVO<sub>4</sub> crystal nuclei. The Bi<sup>3+</sup> and VO<sub>3</sub><sup>-</sup> will grow up into more stable thermodynamic monoclinic BiVO<sub>4</sub> crystal grains according to certain spatial configurations and then irregular monoclinic BiVO<sub>4</sub> in the microwave hydrothermal process [12]. The Zeta potentials of  $Er^{3+}$ -doped BiVO<sub>4</sub> (4-12at.%) are 35.71, 32.76, 32, 10.09, 1.94, respectively, suggesting the decreasing electrostatic repulsion, which can form a large number of BiVO<sub>4</sub> crystal nuclei. The crystal nucleus will generate amorphous BiVO<sub>4</sub> precipitate, which can be crystallized into tetragonal BiVO<sub>4</sub> and  $Er_8V_2O_{17}$  in the drying oven at 80°C (Fig. 1(d)). The tetragonal BiVO<sub>4</sub> and  $Er_8V_2O_{17}$  are dissolved and crystallized into the tetragonal  $Er^{3+}$ -doped BiVO<sub>4</sub> crystal grains with recrystallization process (Tab. 1), resulting in the widened diffraction peak with the To further analyze the crystal structure of the  $Er^{3+}$ -doped BiVO<sub>4</sub>, the Rietveld refinement on the XRD patterns of pure BiVO<sub>4</sub> and the  $Er^{3+}$ -doped BiVO<sub>4</sub> (8at.%) is performed using the Maud program [13, 14]. In the light of the refinement results, the schematics of the BiVO<sub>4</sub> crystal structure are shown in Fig. 1(b). The structural transition of  $Er^{3+}$ -doped BiVO<sub>4</sub> can be found, where the monoclinic BiVO<sub>4</sub> and the  $Er^{3+}$ -doped BiVO<sub>4</sub> (8at.%) having C2/c:c3 and I41/amd:2 space groups, respectively, can be observed.



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Samples	Crystal	Space	Lattice parameters	tetragonal
	structure	group		crystallite size
				(nm)
Undoped	Monoclinic	C2/c:c3	a=5.1881Å b=5.0788Å	
			c=11.6757Å	
4at.% Er <sup>3+</sup>	Tetragonal		a=b=7.2769Å c=6.4413 Å	67.9
6at.% Er <sup>3+</sup>	Tetragonal		a=b=7.2854Å c=6.4424 Å	69.4
8at.% Er <sup>3+</sup>	Tetragonal	I41/amd:2	a=b=7.2894Å c=6.4464Å	69.1
10at.% Er <sup>3+</sup>	Tetragonal		a=b=7.2876Å c=6.4468Å	59.3
12at.% Er <sup>3+</sup>	Tetragonal		a=b=7.2852Å c=6.4465 Å	49.4





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The morphologies of the samples synthesized by microwave-hydrothermal process were characterized by a scanning electron microscopy (SEM), as shown in Fig. 2. When the content of  $Er^{3+}$  is 0 at%, the crystal possesses irregular flake-like morphology with 100 nm thickness (Fig. 2 (a)). The distribution of crystal grains is nonuniform and the gain surface is smooth, resulting in small specific surface area  $(3.25m^2/g)$ . With the increase of doping Er<sup>3+</sup> content (4-12at.%), the flake-like crystal grains are dissolved gradually and recrystallized to the well-defined rod-like crystals of the tetragonal BiVO<sub>4</sub> (Fig. 2(b)-(f)). This implies that the formation of crystals in nucleation-dissolutionrecrystallization may be predominated by  $Er^{3+}$  ions. The increase of the specific surface area (from 7.42  $m^2/g$  to 11.96  $m^2/g$ ) can therefore be correlated with these changes of the morphology and smaller gain size. The changes of morphologies and the specific surface area attribute to the different Zeta potentials, resulting in the different growth of  $BiVO_4$ crystal. The tetragonal BiVO<sub>4</sub> and  $Er_8V_2O_{17}$  crystals are dissolved gradually and recrystallized to form the well-defined rod-like crystals. These results are in accordance with the XRD patterns.



Fig. 3

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It can also be seen in the TEM images that the irregular flake-like crystal is the monoclinic BiVO<sub>4</sub> (0at.%) with 100nm thickness (Fig. 3(a)) and the rod-like crystal is  $Er^{3+}$ -doped BiVO<sub>4</sub> (8at.%) with the length of 300nm (Fig. 3(c)). From the insets in Fig. 3(b) and (d), the SEAD diffraction patterns are the bright spots of electron diffraction, which indicates that both monoclinic and tetragonal BiVO<sub>4</sub> are crystalline. The HRTEM images obtained from the (b) and (d) areas marked with rectangles are shown in Fig. 3(b) and (d). An interval of 0.2910 nm between the uniform fringes is in good agreement with the (040) lattice plane of monoclinic BiVO<sub>4</sub>. Meanwhile, the spaces of 0.4810 nm and 0.3626 nm of the clear lattice fringes with corresponding to (101) and (200) planes of tetragonal BiVO<sub>4</sub> imply the high crystallinity. These results are consistent with the initial XRD analyses.



The optical properties of monoclinic BiVO<sub>4</sub> and  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> are measured by using UV-vis diffuse reflection spectrum in the wavelength range of 200-800nm. From the diffuse reflectance spectra (Fig. 4(a)), two clear absorption edges can be noticed both in the UV and visible light regions, which corresponds to the band gap energy of 2.4 eV and 2.9 eV of the monoclinic and tetragonal phases, respectively [15]. Compared with the monoclinic BiVO<sub>4</sub>, three new absorption bands at ca. 490, 524 and 655 nm of  $Er^{3+}$ -doped BiVO<sub>4</sub> can be observed, which can be assigned to the  $Er^{3+}$ transitions from the <sup>4</sup>I<sub>15/2</sub> ground state to <sup>4</sup>F<sub>7/2</sub>, <sup>2</sup>H<sub>11/2</sub>, and <sup>4</sup>F<sub>9/2</sub> states, respectively [16].

In order to understand the luminescent property of  $Er^{3+}$  doping in the catalysts, we have performed the upconversion fluorescence spectra of  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> (8at.%) upon 980nm laser excitation (Fig. 4(b)). In the spectrum, there are two emission parts: the green emission from 490 nm to 570 nm is corresponding to the transitions from  ${}^{2}H_{11/2}/{}^{4}F_{7/2}$  to  ${}^{4}I_{15/2}$  when  $Er^{3+}$  ions are doped and the red one in a range 640-690 nm is assigned to the transition of  ${}^{4}F_{9/2}$ - ${}^{4}I_{15/2}$  when  $Er^{3+}$  ions are doped [17]. The result indicates the existence of the upconversion process in the  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> photocatalyst. Generally, the  $Er^{3+}$ -doped upconversion process can increase the number

of incoming photons with adequate energy. Then the photons can be absorbed by the photocatalyst, which will generate more photogenerated electron-hole pairs [18]. Therefore, the photocatalytic activities of  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> with up-conversion effect are expected to be efficiently enhanced.



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The photocatalytic activities of the  $Er^{3+}$ -doped BiVO<sub>4</sub> are evaluated by measuring the degradation of RhB aqueous solution under visible light irradiation shown in Fig. 5(a). For the monoclinic BiVO<sub>4</sub>, the photodegradation of RhB is 63.13% after 150min irradiation. By introducing the up-conversion  $Er^{3+}$  and optimizing the contents (4-12at.%), the photodegradation rates of RhB have promptly reached to 96.80%, 96.98%, 97.2%, 96.38% and 88.35% respectively, which exhibits much higher photocatalytic activity than that of the monoclinic BiVO<sub>4</sub>. When  $Er^{3+}$  is increased to 10at.%, the photocatalytic

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activity begins to be decreased because the excessive  $\text{Er}^{3+}$  ions may cover the active sites on BiVO<sub>4</sub> surface and also may act as the recombination centers of photogenerated electrons and holes, resulting in the decrease of photocatalytic activity [19]. Therefore, the optimum content of doping  $\text{Er}^{3+}$  is 8at.%.

The temporal evolution of spectral changes during the photodegradation process of RhB for  $Er^{3+}$ -doped BiVO4 (8at.%) is displayed in Fig. 5(b). From the spectra, it can be seen that the absorbance of RhB at the maximum absorption wavelength is gradually decreased, which realizes the de-ethylation. Under visible illumination, the intense bright cherry-red color of the starting solution gradually disappears with increasing exposure time. The de-ethylation of the N, N, N, N-tetraethylated rhodamine molecules appears in the wavelength position of its major absorption band moving toward the blue region, and it is as follows: λmax, RhB, 554 nm; N, N, N-triethylated rhodamine, 539nm; N, N-diethylated rhodamine, 522nm; and N-ethylated rhodamine, 510nm; and rhodamine, 498nm. RhB has completely been changed into rhodamine [20]. Then through the destruction of their conjugate structure, the further degradation is achieved. After a series of complicated oxidation reaction, the RhB is decomposed to smaller organics and minerals, which can be proved by the results of the TOC measurement [21]. The inset in Fig. 5(b) displays that the ability of Er<sup>3+</sup>-doped tetragonal BiVO<sub>4</sub> (8at.%) to mineralize RhB is evaluated by monitoring changes of organic carbon in TOC. As can be seen, TOC diminishes gradually and ca. 36% TOC removal is obtained after 150 min irradiation, implying that RhB degradation is accompanied by partial mineralization.

The recycle experiments are performed to evaluate the photocatalytic repeatability

and stability of  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> (8at.%) photocatalyst under visible light irradiation [22]. Fig. 5(c) shows the results from the four successive runs of the photodegradation of RhB under the same experimental conditions. It is clear to see that no significant photoactivity loss is observed after four times of successive recycles. The results indicate that  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> (8at.%) photocatalyst is stable during the photodegradation of RhB.

Fig. 5(d) shows the mechanism of the upconversion of  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub>. For monoclinic BiVO<sub>4</sub>, the absorbable light is limited to 519 nm (Fig. 4(a)), while the proper doping content of  $Er^{3+}$  in the  $Er^{3+}$ doped BiVO<sub>4</sub> with can effectively be converted from the long wavelength light to the short wavelength light so as to generate the excited electrons with higher energy and sequentially to capture low energy photons as shown in Fig. 5(d). When these excited electrons are on the ground state by means of irradiation or energy transformation, the emitted light or the transformed energy will make the tetragonal BiVO<sub>4</sub> yield more photoinduced electron-hole pairs so as to enhance the photocatalytic activities. Then the highly oxidative holes accumulated in the BiVO<sub>4</sub> can directly decompose the organic pollutants or react with H<sub>2</sub>O molecules to produce •OH [23, 24], which indicates that the upconversion process can enhance the utilization of efficient photons of  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> photocatalysts. On the basis, the upconversion plays a significant role in the improvement of the photocatalytic activities in the  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> system.

# 4. Conclusions

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The tetragonal BiVO<sub>4</sub> with different  $Er^{3+}$ -doped contents has been successfully synthesized by microwave hydrothermal method. The morphology of  $Er^{3+}$ -doped BiVO<sub>4</sub> has been changed from irregular flake-like to rod-like crystals with the structural transition from monoclinic to tetragonal BiVO<sub>4</sub>. Compared with the monoclinic BiVO<sub>4</sub>, the upconversion of the  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> occurs through the transitions from the <sup>4</sup>I<sub>15/2</sub> ground state to <sup>4</sup>F<sub>7/2</sub>, <sup>2</sup>H<sub>11/2</sub>, and <sup>4</sup>F<sub>9/2</sub> states, which makes the tetragonal BiVO<sub>4</sub> generate more photoinduced electron-hole pairs so as to enhance the photocatalytic activities. Furthermore, the  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> exhibits significantly higher photocatalytic activity than that of the monoclinic BiVO<sub>4</sub> for the degradation of RhB under visible light irradiation.

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# **Figure Captions**

Fig. 1 (a) XRD patterns of different  $Er^{3+}$ -doped contents. (b) Rietveld refined XRD patterns and the insets show schematics of the monoclinic BiVO<sub>4</sub> and  $Er^{3+}$ -doped BiVO<sub>4</sub> (8at.%). (c) Zeta potential of different  $Er^{3+}$ -doped contents. (d) XRD patterns of monoclinic BiVO<sub>4</sub> and  $Er^{3+}$ -doped BiVO<sub>4</sub> (8at.%) in the drying oven at 80°C.

Fig. 2 SEM images of  $Er^{3+}$ -doped BiVO<sub>4</sub> (a) 0at.% (b) 4at.% (c) 6at.% (d) 8at.% (e) 10at.% (f) 12at.%. (g) Specific surface areas of the monoclinic BiVO<sub>4</sub> and  $Er^{3+}$ -doped BiVO<sub>4</sub>.

Fig. 3 (a, b) TEM images and HRTEM of monoclinic  $BiVO_4$  (0at.%); (c, d) TEM images and HRTEM of  $Er^{3+}$ -doped  $BiVO_4$  (8at.%) (the insets in (b) and (d) show SEAD patterns).

**Fig. 4 (a)** UV-vis diffuse reflection absorption spectra of  $Er^{3+}$ -doped BiVO<sub>4</sub>. (b) The upconversion fluorescence spectra of  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> (8at.%) upon 980nm laser excitation.

**Fig. 5 (a)** Photocatalytic degradation to RhB with different  $Er^{3+}$  doping contents; **(b)** absorption spectra changes during the photocatalytic degradation of the  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> (8at.%) in RhB solution under visible light irradiation (inset show the TOC analysis of the degradation of RhB solution by the  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> (8at.%) photocatalyst) **(c)** Cycling runs in the photocatalytic degradation of RhB in the presence of  $Er^{3+}$ -doped tetragonal BiVO<sub>4</sub> (8at.%) photocatalyst. **(d)** A schematic illustration of the energy conversion in the  $Er^{3+}$ -doped BiVO<sub>4</sub> photocatalyst.

Tab. 1 Rietveld refined structural parameters and crystallite size of the catalysts.