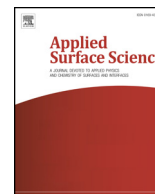




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Full Length Article

# Engineering of Gd/Er/Lu-triple-doped Bi<sub>2</sub>MoO<sub>6</sub> to synergistically boost the photocatalytic performance in three different aspects: Oxidizability, light absorption and charge separation

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## ABSTRACT

Lanthanide doping is an effective and controllable approach for optimizing the oxidation ability, light absorption and charge separation of photocatalysts. However, the multiple drawbacks of mono-component photocatalysts have not been adequately resolved by the doping of only one or two lanthanide ions. Herein, a novel Gd/Er/Lu-triple-doped Bi<sub>2</sub>MoO<sub>6</sub> photocatalyst was synthesized using a hydrothermal method. The results of trapping and 4-Chlorophenol degradation experiments suggested that the oxidizing efficiency of Bi<sub>2</sub>MoO<sub>6</sub> was clearly enhanced by the generation of hydroxyl radicals after doping with the Gd<sup>3+</sup> redox centers. The obtained diffuse reflectance spectra demonstrated that introducing Er<sup>3+</sup> ions provides energy upconversion centers to improve light absorption. The obtained X-ray photoelectron and photoluminescence spectra demonstrated that abundant oxygen vacancies were produced in the Bi<sub>2</sub>MoO<sub>6</sub> crystal after the doping of Lu<sup>3+</sup> ions, contributing to promoting the separation of charge carriers. In summary, Gd/Er/Lu-triple-doped Bi<sub>2</sub>MoO<sub>6</sub> displays much better photocatalytic performance than single- and double-doped Bi<sub>2</sub>MoO<sub>6</sub> materials, which is attributed to the synergistic effects of the Gd<sup>3+</sup>, Er<sup>3+</sup> and Lu<sup>3+</sup> ions. These discoveries demonstrate a novel synergistic effect of the redox centers (Gd<sup>3+</sup> doping), energy upconversion (Er<sup>3+</sup> doping) and oxygen vacancies (Lu<sup>3+</sup> doping) for the design and fabrication of high-efficiency photocatalysts.

## 1. Introduction

Semiconductor photocatalysis is a promising and green technology with tremendous potential for decomposing organic contaminants, reducing CO<sub>2</sub>, splitting water, and purifying air pollutants [1–7]. Various kinds of photocatalysts, including oxysalts, metal sulfides, metal oxides, metal halides, and carbides, have been developed over the last few decades [8–14]. Nevertheless, weak oxidizability, poor light absorption and high charge carrier recombination rates have limited the practical applications of almost all of these single-component photocatalysts in organic contaminant degradation [15]. An intense research effort has been focused on modifying the single-component photocatalysts by various different approaches in order to solve these problems. These approaches mainly include three aspects: fabricating heterojunction photocatalysts with other semiconductors [16–19], loading cocatalysts [20–22], and doping with metal or nonmetal ions [23–26]. The results obtained for modified photocatalysts indicate that among the three problems of oxidation ability, light absorption range and charge separation, either one or two of these problems have been ameliorated,

which could result in a high-efficiency photocatalytic performance.

Doping is a controllable and convenient modification method for importing the dopants into the crystal structure that can address the problematic oxidizability, light absorption or charge carrier recombination rate by acting through three different pathways, thereby enhancing the activity of the photocatalyst [2,27]. These pathways mainly include three aspects. The first is focused on facilitating the separation of the photogenerated charge carriers by forming oxygen vacancies or built-in redox centers in the crystalline structure [28,29]. The second is the extension of the light absorption edge by introducing upconversion dopants to convert visible light into ultraviolet light, or introducing doping levels to narrow the bandgap of the photocatalyst [30,31]. The latest emerging approach has focused on improving the oxidizability for organics degradation by producing a hydroxyl radical by the doping of the Gd<sup>3+</sup> redox centers [32]. Nevertheless, the multiple drawbacks of the single-component photocatalysts have not been adequately resolved by introducing only one kind of ion. Recent studies have clearly shown that more efficient photocatalysts can be obtained by codoping with two elements that can achieve more than one effect

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due to a synergistic effect of the two elements, such as the synergistic effect of the redox centers and doping levels in the Sm/N-codoped  $\text{Bi}_2\text{WO}_6$  [33], the synergistic effect of upconversion and doping levels in the Er/Al-codoped  $\text{ZnO}$  [34], and the synergistic effect of the  $\text{Gd}^{3+}$  redox centers and oxygen vacancies (W doping) in the Gd/W-codoped  $\text{Bi}_2\text{MoO}_6$  [35]. Therefore, the development of a new synergistic effect of three different pathways by the simultaneous doping of three appropriate ions may be a feasible and effective approach to enhance the photocatalytic activity, that to the best of our knowledge, has not been reported to date.

In particular, lanthanide elements have been identified as ideal dopants for enhancing the performance of the photocatalysts due to their unique 4f electron configuration and optical properties [36]. Recently, an increasing number of studies have been reported on the use of single-ion doping and codoping with lanthanide ions to achieve a higher photocatalytic performance. These studies indicated that doping the catalysts with one or two lanthanide ions can enhance the oxidizability by producing hydroxyl radicals [32,35], facilitate the charge separation by the built-in redox couples [37,38], or upconvert lower-energy light to high-energy light by multiple energy transfer processes [39,40], thereby enhancing the photocatalytic efficiency. However, the studies on the simultaneous doping of three suitable lanthanide ions into a photocatalyst for developing a new synergistic effect of three different action pathways have not been reported, and the details of the action mechanisms of the three different lanthanide ions are still not understood.

In this study, bismuth molybdate ( $\text{Bi}_2\text{MoO}_6$ ) was chosen as the host material due to its photocatalytic, luminescent and dielectric properties [41]. Gadolinium was used to enhance the oxidizability by generating the  $\cdot\text{OH}$  radicals, erbium was employed to extend the light response region by upconverting visible light into ultraviolet light, and lutetium was chosen to facilitate the charge separation by generating oxygen vacancies [32,42,43]. Thus, a new Gd/Er/Lu-triple-doped  $\text{Bi}_2\text{MoO}_6$  photocatalyst was fabricated using the hydrothermal method. The results of the photocatalytic degradation experiments showed that the Gd/Er/Lu-triple-doped  $\text{Bi}_2\text{MoO}_6$  photocatalyst showed a clearly enhanced photocatalytic performance compared to the pure, single- and double-doped  $\text{Bi}_2\text{MoO}_6$ . The action mechanisms for the synergistic effects of  $\text{Gd}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Lu}^{3+}$  in enhancing the photocatalytic performance of  $\text{Bi}_2\text{MoO}_6$  were also studied in depth.

## 2. Experimental section

### 2.1. Preparation of pure $\text{Bi}_2\text{MoO}_6$ and doped $\text{Bi}_2\text{MoO}_6$ photocatalysts

The pure  $\text{Bi}_2\text{MoO}_6$  and doped  $\text{Bi}_2\text{MoO}_6$  samples were prepared using a facile hydrothermal method. 0.14 mmol  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  and 2 mmol  $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$  were respectively dissolved in 30 mL of deionized water and 40 mL of 2 mol  $\text{L}^{-1}$   $\text{HNO}_3$  solution to be the cleared solutions. Subsequently,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  solution was dropwise added into  $\text{Bi}(\text{NO}_3)_3$  solution, then the obtained suspension of  $\text{Bi}_2\text{MoO}_6$  precursor was stirred for 30 min. Whereafter, a different amount of Gd ( $\text{NO}_3)_3$ , Er ( $\text{NO}_3)_3$  or Lu ( $\text{NO}_3)_3$  solutions were respectively added into the above suspensions, then the pH values of suspensions were adjusted to 9 using dilute  $\text{NH}_3\cdot\text{H}_2\text{O}$  solution. After 30 min strongly stirring, the ultimate mixtures were respectively moved into 100 mL Teflon-lined stainless autoclave. All reactors were heated at 180 °C for 12 h. Finally, the precipitates were collected by suction filtration and washed using deionized water several times, then, they were dried at 80 °C for 6 h. In this experiment, the as-prepared samples were shown below: pure  $\text{Bi}_2\text{MoO}_6$  (pure BMO), 2.0%Gd-BMO (Gd-BMO), 2.0%Er-BMO (Er-BMO), 2.0%Lu-BMO (Lu-BMO), 2.0%Gd/2.0%Er-BMO (Gd/Er-BMO), 2.0%Gd/2.0%Lu-BMO (Gd/Lu-BMO), 2.0%Er/2.0%Lu-BMO (Er/Lu-BMO), and 2.0%Gd/2.0%Er/2.0%Lu-BMO (Gd/Er/Lu-BMO). All the above percentages were the atomic ratio of Ln/Bi (Ln = Gd, Er, or Lu).

### 2.2. Characterization

The crystalline phases of the samples were collected using X-ray diffraction (XRD; D/MAX-RB, Rigaku, Japan). The morphologies and element distribution of the samples were determined using a scanning electron microscope (SEM; SU8010, Hitachi, Japan) equipped with an energy-dispersive X-ray (EDX) spectrometer. The high-resolution transmission electron microscopy (HRTEM) images were collected by a transmission electron microscope (F-20, FEI, USA). The real contents of Bismuth, Gadolinium, Erbium and Lutetium in as-prepared samples were collected by inductively coupled plasma optical emission spectrometry (ICP-OES; 5110, Agilent, USA). X-ray photoelectron spectra of the samples were measured by an X-ray photoelectron spectrometer (XPS; Escalab 250Xi, Thermo, USA) using an Al  $K\alpha$  source. The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the samples were performed using an UV-vis spectrophotometer (T9s, Persee, China). The photoluminescence (PL) spectra of the samples were determined by a fluorescence spectrophotometer (F-7000, Hitachi, Japan). Photoelectrochemical measurement was recorded by using an electrochemical workstation in a traditional three-electrode system (5060F, RST, China). The electron paramagnetic resonance (EPR) spectra were recorded with an EPR spectrometer (JES-FA200, JEOL, Japan). The spectra were obtained by a microwave power of 0.998 mW, a frequency of 9.07 GHz and a central magnetic field of 324.51 mT.

### 2.3. Photocatalytic activity tests

The photocatalytic activities of the samples were evaluated by photodegrading rhodamine B (RhB, 12 mg  $\text{L}^{-1}$ ), tetracyclines (TCs, 20 mg  $\text{L}^{-1}$ ), and 4-Chlorophenol (4-CP, 15 mg  $\text{L}^{-1}$ ) under the irradiation of a 400 W xenon lamp with an optical filter (420 nm) used as the light source. In each experiment, 30 mg of the sample was evenly dispersed in 30 mL of the organic solution by stirring. Prior to the irradiation, the obtained suspension was stirred strongly for 60 min to achieve an adsorption-desorption equilibrium in the dark. During the photoreaction for RhB degradation, about 3.0 mL of the homodispersed suspension was removed every 30 min, while it was removed once per 1 h in the examination of the TCs and 4-CP degradations; then, the withdrawn suspension was centrifuged to obtain the supernatant liquid. The concentrations of the RhB, TCs and 4-CP were analyzed by measuring the absorbance of the supernatant liquid at 553, 357 and 225 nm, respectively, using a T9s spectrophotometer.

## 3. Results and discussion

### 3.1. Analysis of material structures, morphologies, composition and chemical states

X-ray diffraction (XRD) measurements were used to determine the crystal phase, crystallite size and lattice parameters and to study the incorporation of the dopant ions into the BMO lattice. Fig. 1 shows that all of the XRD patterns of the as-prepared samples were consistent with the koechlinite phase of  $\text{Bi}_2\text{MoO}_6$  (JCPDS card no. 21-0102), which demonstrated that the doping of gadolinium, erbium and lutetium did not give rise to the generation of any new phases due to the low concentration of the dopant ions [44]. Rather, it is only observed from Fig. 1 that the peak intensities of the doped samples are reduced compared to those of pure BMO, implying that the degree of cationic ordering was decreased by doping BMO with the  $\text{Gd}^{3+}$ ,  $\text{Er}^{3+}$  or  $\text{Lu}^{3+}$  ions. This result also shows that a fraction of the  $\text{Bi}^{3+}$  ions in the BMO lattice were successfully replaced by the  $\text{Gd}^{3+}$ ,  $\text{Er}^{3+}$  or  $\text{Lu}^{3+}$  ions [41]. As shown in Table 1, the unit cell parameters of all of the obtained samples were calculated using the XRD pattern data in order to study the changes in the crystalline phase due to the doping of the  $\text{Gd}^{3+}$ ,  $\text{Er}^{3+}$  or  $\text{Lu}^{3+}$  ions. It was observed that the crystal volume of the doped samples decreased after the doping of the  $\text{Gd}^{3+}$  or  $\text{Er}^{3+}$  ions due to the

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