

Synthesis of Er-doped Bi₂WO₆ and enhancement in photocatalytic activity induced by visible light

Meng Wang, Ziyu Qiao, Minghao Fang*, Zhaohui Huang*, Yan'gai Liu, Xiaowen Wu, Chao tang, Hao Tang, Hekai Zhu

Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing, 100083

E-mail: fmh@cugb.edu.cn (Minghao Fang); huang118@cugb.edu.cn (Zhaohui Huang). Tel: +861082322186

** Electronic Supplementary Information (ESI) available.*

Electronic Supplementary Information

(Including Experimental, Supplementary figures)

Experimental

Synthesis of Er-doped Bi₂WO₆ photocatalyst

All the chemicals were of analytical grade and were used without further purification. Undoped Bi₂WO₆ and Er-doped Bi₂WO₆ photocatalysts were synthesized under hydrothermal conditions. In a typical process, Na₂WO₄·2H₂O (2.5 mmol) and an appropriate amount of Bi(NO₃)₃·5H₂O were dissolved in 20 mL of distilled water with vigorous stirring to form a suspension (suspension A). Second, a certain amount of Er(NO₃)₃·6H₂O was dissolved in 20 mL of distilled water with vigorous stirring to form a transparent solution (solution B). Solution B was added into suspension A with continuous stirring. After stirring for another 30 min at room temperature, the resulting suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 24 h. Finally, the autoclave was allowed to cool down naturally to room temperature. The products were collected by centrifugation, washed three times by alternating with deionized water and ethanol, and dried in an oven at 80 °C for 10 h. The doping concentrations of Er³⁺ ions were confirmed as 0.5%, 1.0%, 1.5%, 2.0%, and 3% on the basis of the molar percentage of Er in Bi₂WO₆. For the convenience of description, the samples are hereafter referred to as 0.5% Bi₂WO₆:Er³⁺, 1.0% Bi₂WO₆:Er³⁺, 1.5% Bi₂WO₆:Er³⁺, 2.0% Bi₂WO₆:Er³⁺, and 3.0% Bi₂WO₆:Er³⁺. Similarly, undoped Bi₂WO₆ was prepared by the same method.

Characterization

The crystallinity of the photocatalysts thus synthesized was characterized by XRD on a Bruker D8 Advance diffractometer using Cu-K radiation. The morphology of the photocatalysts was examined using a field-emission SEM (FESEM, MERLIN Compact, Germany) operating at an accelerating voltage of 40 kV. XPS spectra were recorded on a VGMPK II XPS (Thermo Fisher ESCALAB 250Xi, USA). PL emission spectra of the photocatalysts were recorded on a fluorescence spectrophotometer (Shimadzu Rf-540, Japan). UV-visible absorption spectra of the photocatalysts were examined on a UV-vis spectrophotometer (Agilent CARY 5000, Australia) with an integrated sphere attachment in the range of 200–800 nm. BaSO₄ was used as the reflectance standard. The photocurrents were recorded on an electrochemical system (CHI 660D, China).

Photocatalytic activity experiments

The photocatalytic activities of the undoped Bi₂WO₆ and Bi₂WO₆:Er³⁺ photocatalysts were evaluated by the degradation reaction of RhB (10 mg/L) under irradiation of visible light ($\lambda > 420$ nm), illuminated by a 500 W xenon lamp. First, 50 mg of the photocatalysts was dispersed by ultrasonication in an aqueous solution of RhB (50 mL, 10 mg/L). Second, the suspensions were magnetically stirred for 60 min in the dark to ensure that an adsorption-desorption equilibrium was attained before irradiation. Next, a 3.0 mL suspension was taken and separated by centrifugation (4500 rpm, 10 min) at certain time intervals. The RhB concentration was tested by recording the absorbance at the characteristic band of 554 nm on an L6 UV-vis spectrophotometer.

Photoelectrochemical measurements

A standard three-electrode cell with a standard calomel electrode (SCE) as the reference electrode, a platinum wire as the counter electrode, and a $\text{Bi}_2\text{WO}_6:\text{Er}^{3+}$ film electrode on ITO as the working electrode were employed in photoelectric studies, and 0.1 M Na_2SO_4 was used as the supporting electrolyte. Potentials were recorded with reference to the SCE. The photoelectric responses of $\text{Bi}_2\text{WO}_6:\text{Er}^{3+}$ were recorded at 0 V when the light was switched on and off. All measurements were conducted at room temperature.

For detecting the active species generated in the photocatalytic process, the following reaction conditions were employed for the photodegradation of RhB: addition of 1 mM ethylenediaminetetraacetic acid disodium salt (EDTA-2Na; quencher of h^+), 1 mM benzoquinone (BQ; quencher of $\cdot\text{O}_2^-$), and 1 mM isopropanol (IPA; quencher of $\cdot\text{OH}$). This trapping experiment was similar to the above photocatalytic activity experiments.

Supplementary figures

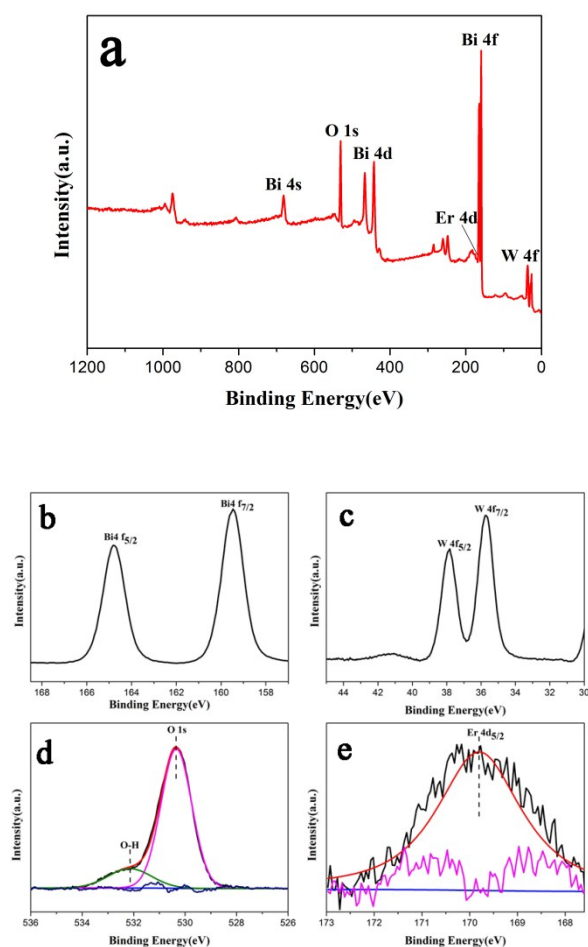


Fig. S1 XPS spectra of the 1.5% $\text{Bi}_2\text{WO}_6:\text{Er}^{3+}$: (a) survey, (b) Bi 4f, (c) W 4f, (d) O 1s, and (e) Er 4d

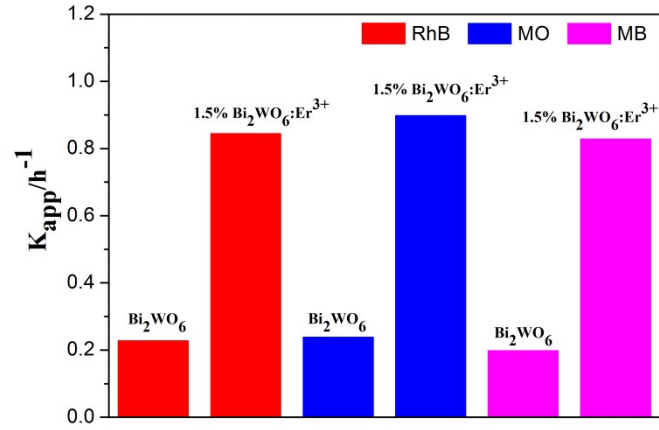


Fig. S2 The comparison of the rate constant k of the degradation of RhB, MO and MB dye

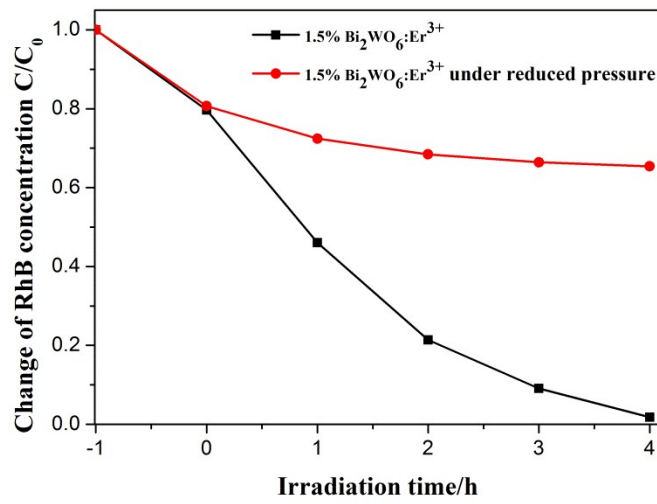


Fig. S3 Photocatalytic degradation curves of RhB over $1.5\% Bi_2WO_6:Er^{3+}$ under air or reduced pressure