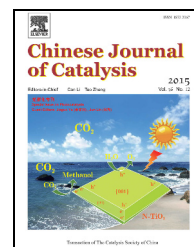


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# Fabrication of a $\beta$ - $\text{Bi}_2\text{O}_3$ / $\text{BiOI}$ heterojunction and its efficient photocatalysis for organic dye removal



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## ABSTRACT

To improve  $\beta$ - $\text{Bi}_2\text{O}_3$  photocatalysis, we couple  $\beta$ - $\text{Bi}_2\text{O}_3$  with  $\text{BiOI}$  to form  $\beta$ - $\text{Bi}_2\text{O}_3$ / $\text{BiOI}$  heterojunctions through an in-situ treatment with hydriodic acid. The prepared heterojunctions are characterized with X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, ultra violet-diffuse reflectance spectroscopy, and X-ray photoelectron spectroscopy. Upon visible-light irradiation ( $\lambda > 420$  nm), the  $\beta$ - $\text{Bi}_2\text{O}_3$ / $\text{BiOI}$  heterojunctions, especially with the molar ratio of HI to  $\beta$ - $\text{Bi}_2\text{O}_3$  at 0.4, exhibit much higher photocatalytic activity than pure  $\beta$ - $\text{Bi}_2\text{O}_3$  and  $\text{BiOI}$  for the degradation of methyl orange. The efficient separation of photogenerated electron-hole pairs across the interface of the heterojunction between  $\beta$ - $\text{Bi}_2\text{O}_3$  and  $\text{BiOI}$  would be responsible for the enhanced photocatalytic performances.

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## 1. Introduction

Environmental pollution and the energy shortage have become two of the biggest challenges currently facing humans. Semiconductor photocatalysis with a primary focus on  $\text{TiO}_2$  is one of the most promising technologies for environmental remediation and energy conversion [1–4]. However, owing to its large band gap of 3.2 eV,  $\text{TiO}_2$  can drive a catalytic reaction only under ultraviolet or near ultraviolet irradiation, which occupies less than 4% of the solar light spectrum on the earth. To make full use of solar light, therefore, the development of narrow band gap semiconductors as efficient visible-light photocatalytic materials has been of particular interest in recent years [5–10]. Bismuth trioxide ( $\text{Bi}_2\text{O}_3$ ), which exhibits a narrow band gap that varies between 2.1–2.8 eV, is a promising candidate as a visible-light photocatalyst owing to its unique characteristics, such as strong absorption in visible region and non-toxic prop-

erty similar to  $\text{TiO}_2$ . It is well-known that  $\text{Bi}_2\text{O}_3$  has six polymorphic forms, including the  $\alpha$  (monoclinic),  $\beta$  (tetragonal),  $\gamma$  (body-centered cubic),  $\delta$  (face-centered cubic),  $\varepsilon$  (tetragonal), and  $\omega$  (triclinic) phases, each with unique physical properties [11]. Among them,  $\alpha$ - $\text{Bi}_2\text{O}_3$ ,  $\beta$ - $\text{Bi}_2\text{O}_3$  and  $\delta$ - $\text{Bi}_2\text{O}_3$ , with photocatalytic activities towards the degradation of organic pollutants, have been reported.  $\beta$ - $\text{Bi}_2\text{O}_3$ , with a relatively narrow band gap (less than  $\sim 2.50$  eV), has been shown to be the most active form for photocatalytic application [12–14]. Nonetheless, their efficiencies are still insufficient for practical application.

The construction of a semiconductor heterojunction by coupling with a secondary substance (noble metal, other semiconductors, and so on) has been proven to be an effective and simple strategy to improve the photocatalytic activity of photocatalysts [15,16]. In the semiconductor heterojunction, several advantages can be achieved: (1) an improvement of the charge

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separation; (2) a long lifetime of the charge carriers; and (3) an enhancement of the charge transfer to the catalyst surface. All these features endow the semiconductor heterojunction with an enhanced photocatalytic performance. To date, many Bi<sub>2</sub>O<sub>3</sub>-based heterojunction photocatalysts have been successfully developed for the efficient degradation of organic pollutants [17–19]. In particular, the heterojunctions between  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> and bismuth oxyhalides (BiOX, X = Cl, Br, or I), formed through an in-situ treatment of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> with HX, such as  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>/BiOI and  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>/BiOCl, exhibit unique advantages not only in photocatalytic performance but also in the fabrication method [20–22]. However, to the best of our knowledge, the heterojunctions between  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> and BiOX (X = Cl, Br, or I) are not yet to be reported. Among the BiOX family, bismuth oxyiodide (BiOI) possesses the smallest band gap (less than 1.8 eV) and strong absorption in the visible region [23]. With the aims of the full use of solar light, improvement in  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> photocatalysis for a practical application, and convenient fabrication features, in this work, we coupled  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> with BiOI to form  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>/BiOI heterojunctions through an in-situ treatment with HI. The prepared  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>-based heterojunctions have been shown to exhibit much higher photocatalytic activities than pure  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> and BiOI for the degradation of methyl orange (MO) upon visible-light irradiation. Furthermore, the mechanism of the enhanced photocatalytic performance over the heterojunctions was also investigated and discussed according to various characterization results.

## 2. Experimental

### 2.1. Sample preparation

$\beta$ -Bi<sub>2</sub>O<sub>3</sub> was synthesized by using Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> as a precursor, as reported in previous work [24]. Initially, 11.64 g of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was dissolved in 60 ml aqueous solution of HNO<sub>3</sub> (1 mol/L). Under constant stirring, 240 ml aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (0.6 mol/L) was slowly added into the solution to produce a large amount of white precipitate. The suspension was further stirred for 15 min and aged at 60 °C for 12 h. Finally, the precipitate was collected and washed several times with deionized water before being dried at 60 °C for 6 h to form the Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> precursor.  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> was obtained by annealing the prepared Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> at 350 °C for 30 min. The  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>/BiOI heterojunctions were prepared by an in-situ treatment of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> with HI. In detail, 0.7 g of the freshly prepared  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> was dispersed into 20 ml of an ethanol and water mixture with the desired amount of HI, which was prepared by changing the amount of the aqueous solution of HI (45%). To obtain the  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> based heterojunctions with different amount of BiOI, the molar ratios of HI to  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> ( $R_{HI}$ ) in the dispersions were controlled at 0.2, 0.4, and 0.8, respectively. The dispersion was stirred and sonicated for 30 min at room temperature. After the treatment with HI, the precipitate was recovered by centrifugation, washed several times with ethanol, and finally dried at 80 °C in air for 10 h. By following this procedure, the pure BiOI was synthesized in the presence of HI in excess. For comparison, the pure  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> was also treated in the same manner in

the absence of HI.

### 2.2. Characterization

The polycrystalline X-ray diffraction (XRD) patterns of the prepared samples were recorded with an X-ray diffractometer (Shimadzu, XRD-7000) using Cu  $K_{\alpha}$  ( $\lambda = 1.5406 \text{ \AA}$ ) as X-ray radiation with an applied potential of 40 kV and electron beam current of 30 mA. Ultra violet-visible diffuse reflectance spectroscopy measurements were carried out on a UV-Vis spectrometer (Hitachi U-4100) equipped with a diffuse reflectance accessory. Field-emission scanning electron microscopy (FESEM) observations were performed with a JEOL 6701F microscope. High-resolution transmission images (HRTEM) were taken using a JEOL JEM-2010 electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a XPS system (ESCALAB 250Xi) with a 300 W Al  $K_{\alpha}$  source. All binding energies were referenced to the C 1s peak (284.6 eV) of surface adventitious carbon. Photoluminescence (PL) spectra were obtained on a Hitachi F-4600 spectrophotometer with an excitation wavelength at 380 nm.

### 2.3. Evaluation of photocatalytic activity

MO was chosen as a model pollutant to evaluate the photocatalytic activities of the prepared pure Bi<sub>2</sub>O<sub>3</sub>, BiOI, and  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>/BiOI heterojunctions under visible-light irradiation ( $\lambda > 420 \text{ nm}$ ). In a typical photocatalytic experiment, 0.1 g of the catalyst was dispersed in 100 ml aqueous solution of MO ( $4 \times 10^{-5} \text{ mol/L}$ ). The light source was a 300 W Xe-arc lamp (CHF-XM150, Beijing Trusttech. Co. Ltd.) equipped with a glass filter ( $\lambda > 420 \text{ nm}$ ) to remove the UV wavelength light, and positioned about 8 cm above the aqueous suspension. Prior to irradiation, the suspension was magnetically stirred in the dark for 1 h to reach an adsorption-desorption equilibrium between the catalyst surface and MO molecules. At the given irradiation time intervals, 3 ml of the suspension was sampled and separated by centrifugation before analysis using a Hitachi U-3310 spectrophotometer. The intensity change in the characteristic absorption peak of MO at 461 nm was measured to evaluate the extent of MO degradation.

To investigate the photocatalytic degradation route of MO over these catalysts, triethanolamine (TEOA, 10 mmol/L), as an effective hole scavenger, and tert-butyl alcohol (TBA, 10 mmol/L), as  $\bullet$ OH radical scavenger, were chosen to participate in the photocatalytic degradation of MO over these catalysts. Determination of MO concentration during the photocatalytic reaction in the presence of TEOA or TBA was also conducted by measuring the absorption of MO solution at 461 nm.

## 3. Results and discussion

### 3.1. Phase structure and morphology

Polycrystalline XRD was used to identify the phase structures and constitutions of the prepared samples. The XRD patterns of the prepared samples are illustrated in Fig. 1. It can be

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