



Tuning the physicochemical property of BiOBr via pH adjustment: Towards an efficient photocatalyst for degradation of bisphenol A

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ABSTRACT

The initial pH value of hydrothermal reaction has a significant impact on the photocatalytic activity of BiOBr photocatalyst; however, the influence mechanism is still unclear. In this work, a series of BiOBr photocatalysts were prepared via a hydrothermal route at different initial pH values. Various methods were performed to investigate the effects of pH on the structure, composition, morphology, optical and electronic properties of the as-prepared samples. The results indicated that the increasing pH facilitated the nucleation of BiOBr, leading to the decrease of crystallite size. Moreover, due to the change of {001} facets exposure, the BiOBr nanosheets rotated to reduce the total surface energy of crystal and formed looser structure, even assembled into flower-like structure at pH 7. The photocatalytic activity evaluated by the degradation of bisphenol A (BPA) was positively correlated with the initial pH value. The BiOBr obtained at pH 7 exhibited the highest photocatalytic activity, whose rate constant was about 2.9, 1.9 and 1.5 times than that of BiOBr samples prepared at pH 1, 3 and 5, respectively. The enhanced photocatalytic activity of BiOBr was mainly attributed to the smaller crystallite size and looser structure.

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1. Introduction

Photocatalytic technology is generally considered as a promising strategy to address the issues of energy crisis and environmental pollution, and semiconductor materials are ideal photocatalysts to achieve this strategy [1–3]. However, the photocatalytic efficiency of current photocatalyst is still too low, thus the development of high-performance photocatalyst is vital to meet the demand of industrial application. Since the photocatalytic performance is closely related to the physicochemical property of photocatalyst, considerable attention has been paid to the controllable synthesis of photocatalyst [4–6]. The most common strategy is controlling the synthesis conditions, such as pH value [7], temperature and time conditions [8].

Especially, tuning the pH value of synthetic reaction has been confirmed as an effective and convenient way to improve the photocatalytic performance of catalyst. The photocatalytic activities of various photocatalysts, such as TiO₂ [9], ZnO [10], WO₃ [11], Bi₂MoO₆ [12] and BiVO₄ [13] were enhanced by adjusting the pH

value of synthetic reaction. Furthermore, these previous studies have revealed that pH adjustment is a valid approach to optimize the physicochemical property of catalyst. For instance, Yu et al. prepared high-performance TiO₂ powders with small crystallite size, large specific surface area and mesoporous structure by tuning the initial pH [9]. Tan et al. synthesized ms-BiVO₄ powders with high specific surface area by varying the pH value of precursors [13]. It can be inferred that the initial pH value of synthetic reaction has an important effect on the physicochemical properties of photocatalyst, thus the photocatalytic activity also would change.

Recently, bismuth oxyhalide (BiOX, X = F, Cl, Br, I) has attracted extensive attention due to its intrinsic layer structure, broad ranged band gap and high chemical stability, which endow it with excellent photocatalytic performance in the degradation of organic pollutants [14]. In particular, bismuth oxybromide (BiOBr) stimulated great research interest because of its suitable band gap and relatively superior visible-light photocatalytic activity. The influence of the initial pH value of synthetic reaction on photocatalytic activity has been reported in the field of BiOX in the last few years. These studies mainly discussed the contribution of exposed facet [15], crystallite size [16] and thickness [17] to the enhanced photocatalytic activity of BiOBr nanosheets. However, those reports have seldom discussed the influence mechanism of pH on these physico-

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chemical properties. Besides, to our knowledge, little attention has been devoted to the influence of pH on the morphological evolution of BiOBr. And there is no consensus on which property contributes most to the photocatalytic performance of BiOBr. Therefore, it is necessary to clarify the influence mechanism of pH value and identify the major impact factor to the photocatalytic activity of BiOBr, which can provide theoretical guidance and effective strategy for controllable synthesis of high-performance photocatalysts.

In this work, a series of BiOBr samples were synthesized via a hydrothermal route at different pH values of synthetic reaction. The structure, composition, morphology, optical and electronic properties of the as-prepared samples were investigated by various characterization techniques. The influence mechanism of initial pH value on the physicochemical properties was discussed, especially the influence of pH on the morphological evolution of BiOBr. Bisphenol A (BPA) was used as model pollutant to evaluate the effect of initial pH value on the photocatalytic activities of BiOBr samples. Moreover, this work also estimated the contribution of different properties and identified the major impact factor to the enhanced photocatalytic activity of BiOBr photocatalyst.

2. Experimental

2.1. Catalysts preparation

BiOBr photocatalysts were prepared via a facile hydrothermal route on the basis of previous studies [18]. All chemicals were commercially available and used without further purification. In a typical synthetic procedure, 6 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 10 mL of HNO_3 solution, and 9 mmol NaBr was dissolved in 60 mL deionized water. Then the $\text{Bi}(\text{NO}_3)_3$ solution was added slowly into the NaBr solution. The pH values of four same dispersions, obtained in the same way described above, were adjusted to 1.0, 3.0, 5.0, and 7.0 by adding aqueous NaOH, respectively. Afterward, the mixtures were stirred adequately and transferred into 100 mL Teflon-lined stainless autoclaves, heated at 160 °C for 12 h under autogenous pressure, then cooled to room temperature. The obtained precipitations were filtered, washed with deionized water and ethanol, and dried in air at 50 °C overnight. The products synthesized at different pH values were denoted as BOB-1, BOB-3, BOB-5 and BOB-7, respectively. It should be emphasized all of the experimental condition are same except the initial pH value.

2.2. Characterization

The crystalline phases were confirmed by X-ray diffraction (XRD, PANalytical X'Pert Pro) with $\text{Cu } \alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and the 2θ ranged from 5° to 80°. X-ray photoelectron spectroscopies (XPS) were conducted on a Thermo Fisher Scientific Escalab 250Xi spectrometer to determine the surface electronic states. The crystallite size and morphology were observed by a field emission scanning electron microscope (FESEM, Hitachi SU8010) and a transmission electron microscope (TEM, JEOL JEM-2010). The specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) model and the pore size distributions were analyzed using the Barrett-Joyner-Halenda (BJH) method from the adsorption branch of the N_2 adsorption-desorption isotherm. UV-vis diffuse reflectance spectra (UV-vis DRS) were acquired using a Pgeneral TU-1901 spectrophotometer, with a BaSO_4 reference. Photoluminescence (PL) spectra were detected under an excitation wavelength of 260 nm by a HORIBA Aqualog spectrofluorometer.

2.3. Photocatalytic activity test

The photocatalytic activities of the BiOBr samples were evaluated by the degradation of BPA aqueous solution under visible-light

irradiation. Experiments were carried out in a double-walled reactor and cooled by circulating water. The visible light was provided by a 300 W Xe lamp with a 420 nm cut off filter, which was placed 20 cm away from the reactor. In each experiment, 50 mg catalyst was added into 100 mL of BPA solution (10 mg/L). Prior to illumination, the suspension was sonicated for 10 min and magnetically stirred in the dark for 30 min to achieve the absorption-desorption equilibrium. At given time intervals, 3 mL of the suspension was withdrawn and centrifuged at 10,000 rpm for 5 min to remove the particles. The supernatant was filtered through a 0.45 μm membrane filter and determined by a HPLC instrument (LC-2010A HT, Shimadzu). The HPLC analysis was carried out using an Inertsil ODS-SP column and UV-vis detector at 276 nm, with acetonitrile and water (65/35, v/v) as mobile phase at a flow rate of 1.0 mL/min. The total organic carbon (TOC) was detected with a TOC analyzer (TOC-V CPH, Shimadzu) to investigate the mineralization degree of the pollutants.

2.4. Electrochemical measurement

The transient photocurrent response of BiOBr samples were measured with amperometric I-t curve method using an electrochemical analyzer (CHI660D, Shanghai) in a standard three-electrode system. BiOBr photoanode ($1 \times 1 \text{ cm}^2$), platinum plate and Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. An aqueous solution of 0.1 M Na_2SO_4 was used as electrolyte. For preparing photoanode, 20 mg of BiOBr powder, 20 μL of Nafion solution (D520, DuPont) and 1 mL of *N,N*-dimethylformamide (DMF) were mixed and stirred for 10 min. The resulted paste was spread evenly on a fluorine-tin oxide (FTO) glass and dried at 60 °C.

3. Results and discussion

3.1. Physicochemical property

Since the performance of photocatalyst mainly depends on its physicochemical properties, the structure, composition, morphology, optical and electronic properties of BiOBr samples were investigated systematically, thereby having a deep insight into the influence mechanism of pH value.

3.1.1. Structure and composition

Fig. 1a shows the XRD patterns of the as-prepared BiOBr photocatalysts. The intense and clear diffraction peaks implied the good crystallinity of the samples. All the peaks could be indexed to the pure tetragonal BiOBr (JCPDS 78-0348). However, due to the competitive relationship between the OH^- and Br^- in basic solution [19], further increasing of pH value to basic condition led to the formation of impurity, such as $\text{Bi}_{24}\text{O}_{10}\text{Br}_{31}$ (Fig. S1). Therefore, the pH values were controlled no more than 7 to obtain the exclusive product of BiOBr. Moreover, it is noteworthy that the (001), (002), (003) and (004) diffraction peaks (marked with "*" in Fig. 1a) weakened with increasing pH, indicating the reduced exposure percentage of {001} facets. This downward trend was further confirmed by the increasing intensity ratios of (110) and (200) to (001) peaks (Fig. 1b), which was consistent with previous work [17]. According to published reports, the {001} facets of BiOBr have a high surface energy and a high density of terminated oxygen atoms, which can have strong binding interaction with H^+ ions, thereby the presence of H^+ ions favors the exposure of {001} facets [20]. So when the concentration of H^+ ions was reduced with increasing pH value, the exposure percentage of {001} facets dwindled because of the weaker binding interaction and principle of low total surface energy.

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