



Original article

Hierarchical BiOBr microspheres with oxygen vacancies synthesized via reactable ionic liquids for dyes removal



Zhi-Dong Wei, Rui Wang*

School of Environmental Science and Engineering, Shandong University, Jinan 250199, China

ARTICLE INFO

Article history:

Received 18 February 2016

Received in revised form 4 March 2016

Accepted 9 March 2016

Available online 16 March 2016

Keywords:

BiOBr

Dyes removal

Photocatalytic

Ionic liquids

Oxygen vacancies

ABSTRACT

Hierarchical BiOBr microspheres with oxygen vacancies, which can be used for the dyes removal, have been synthesized successfully in the presence of different kinds of ionic liquids. It was revealed that BiOBr prepared by the ionic liquids with short chain length exhibited higher photocatalytic activity in the degradation of methyl orange (MO) under visible light. The experimental results showed that the phenomenon of the photocatalytic degradation of MO can be explained by the photoluminescence spectra.

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1. Introduction

Numerous studies have shown that TiO_2 has been extensively investigated as the promising state-of-the-art photocatalysts due to their strong oxidizing ability, low toxicity, low cost, and facile synthesis since it was reported in 1972 [1,2]. However, the photocatalytic efficiency of TiO_2 must overcome the poor quantum yield of the catalyst, which was caused by the rapid recombination of the photogenerated electrons and holes [3,4]. Several research approaches have committed to exploring the more efficient and active photocatalysts.

Recently, BiOBr catalysts have attracted much attention because the hybridization between O_{2p} and Bi_{6s} states narrows the band gap well and enables BiOBr make use of visible light [5]. Furthermore, it has good chemical stability and being eco-friendly [6,7]. BiOBr was a significantly V–VI–VII ternary semiconductor with layer structure characterized by $[\text{Bi}_2\text{O}_2]^{2+}$ slabs that interleaved by double halide atoms layers. Several studies have been reported for the application and preparation of BiOBr micro/nanostructures. Deng *et al.* reported the synthesis of one-dimensional (1D) BiOBr nanowires and nanotubes using a cationic surfactant cetyltrimethylammonium bromide (CTAB) as the bromine source [8]. Two-dimensional (2D) single-crystalline BiOBr nanoplates, nanosheets, and microspheres were obtained by hydrogen peroxide oxidation of bulk metal Bi

particles in a surfactant-mediated solution [9]. Fabrication of three-dimensional (3D) BiOBr materials are more sophisticated. Zhang *et al.* successfully synthesized the 3D flower-like hollow microsphere, which showed a more excellent photoactivity under visible light than the BiOBr bulk plates [10]. In addition, the applications of BiOBr are also various. Jiang *et al.* designed flake-like BiOBr using a HAC-assisted hydrothermal route for photocatalytic degradation of MO [11]. Mesoporous 3D BiOBr microspheres were got by a facile solvothermal method for photodecomposition of toluene [12]. Ai and co-workers found the BiOBr microspheres, which displayed efficient photocatalytic activity, can remove the textile NO species in indoor air [13]. Thus, preparing the BiOBr with different structures that possess visible photocatalytic activity is a new trend nowadays.

Ionic liquids (ILs) are non-volatile and non-flammable organic salts with low melting points [14]. Because of its unique properties, such as extremely low volatility, high ionic conductivity, good dissolving ability and designable structures, it has been widely used as solvents, templates, or reactants for the synthesis of inorganic nanomaterials [15–18]. In 2000, Dai and co-workers first observed the synthesis of SiO_2 aerogel using ionic liquids, which exhibited superior capability for solvation [19]. Khatri *et al.* reported that ultrafine monodisperse gold nanoparticles (AuNPs) were synthesized by an elegant sputtering of gold onto 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid [20]. Xia *et al.* initially prepared the hollow and porous BiOBr materials with ionic liquids, which expanded the methods of the preparation of BiOBr [21].

Although there is much improvement in the area of BiOBr assisted by ionic liquids, the development of more environmental

* Corresponding author.

E-mail address: wangrui@sdu.edu.cn (R. Wang).

friendly and convenient synthesis method is still significantly important for BiOBr. Hence, synthetic conditions remain to be expanded. In addition, it is of great realistic meaning to boost the photocatalytic performance of BiOBr by exploring the conditions of prepared.

In this work, we have synthesized the BiOBr catalysts via an ionic liquid-assisted solvothermal approach to explore the best preparation conditions of dyes removal. Based on this background, BiOBr catalysts have been acquired from different kinds of ionic liquids, which demonstrates that the chain length of ILs have a far-reaching influence on the visible light photocatalytic activity of BiOBr.

2. Experimental

2.1. Materials and physical measurements

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was obtained from Tianjin Bodi Chemical Co., Ltd.; Absolute ethanol, glycol ether were bought from Tinjin Fuyu Chemical Co., Ltd.; ionic liquids was purchased from Shanghai Chengjie Co., Ltd. All of the chemicals are analytic grade and used as received without purification.

X-ray powder diffraction (XRD) analysis was recorded with a Bruker advanced D8 powder diffractometer with a $\text{Cu-K}\alpha$ radiation source. The scan ranges were 10° – 80° with $0.02^\circ \text{ s}^{-1}$, respectively. The morphologies of BiOBr catalysts were observed on a Transmission electron microscopy (SEM). To study the recombination of photo induced charge carriers, photoluminescence (PL, Hitachi F-4500, 250 nm) spectra was collected. Electron Paramagnetic Resonance (EPR) tests were carried out in a magnetic field modulation of 100 kHz using a Bruker, ER 200-SRC spectrometer at 77 K.

2.2. Synthesis of catalysts

Typically, BiOBr was prepared under the conditions of ionic liquids (ILs). The procedure can be concluded as follows. Solution A was formed by the dissolution of 2 mmol of bismuth nitrate pentahydrate in 10 mL of glycol ether. In another process, 2 mmol of 1-butyl-3-methylimidazolium bromide was dissolved in 20 mL of glycol ether. It was denoted as solution B. Solutions A and B were mixed together drop by drop with continuous stirring. When the color of the solution was changed from yellow green to clear and the BiOBr precursor solution was formed, 1 mmol of 1-butyl-3-methylimidazolium bromide was introduced. After stirring for another 1 h, the mixture was transferred into a 50 mL Teflon reactor inside a stainless-steel vessel and heated at 433 K for 8 h. The resulting precipitates were collected, thoroughly washed with deionized water and ethanol three times. After dried at 353 K in the air, the products were got. The particles were denoted as BiOBr- C_4 . Whereas, the course of BiOBr synthesized by ionic liquids of different chain length was followed by the same procedure except that 1-butyl-3-methylimidazolium bromide were substituted by 1-octyl-3-methylimidazolium bromide, 1-dodecyl-3-methylimidazolium bromide and 1-cetyl-3-methylimidazolium bromide in both solution A and B, respectively. The products were marked as BiOBr- C_8 , BiOBr- C_{12} and BiOBr- C_{16} , respectively.

2.3. Photodegradation of dye

The photocatalytic activities of the as-prepared BiOBr samples were tested by photodegradation of methyl orange (MO). Experiments were carried out in a photocatalytic reactor irradiated by a 300 W Xenon lamp with a 420 nm UV light cut filter. In a typical procedure, 0.1 g BiOBr photocatalysts were added into 100 mL of MO aqueous of 10 mg/L. Prior to photocatalytic reaction,

the suspension was magnetically stirred for 30 min in dark to reach an adsorption–desorption equilibrium. Then the mixture was exposed to light irradiation under magnetic stirring. About 4 mL of the suspension was sampled and filtered to remove the photocatalysts every 15 min. The supernatant solution was analyzed by a UV spectrophotometer.

3. Results and discussion

The purity and phase of the samples were determined by X-ray powder diffraction (XRD). Fig. 1 shows the typical diffraction patterns of the as-prepared BiOBr samples under different conditions. For the samples, all the peaks of the as-prepared BiOBr at 25.3° (0 1 1), 31.8° (0 1 2), 32.3° (1 1 0), 46.3° (0 2 0), 57.3° (2 1 2) and 76.7° (0 3 2) were readily indexed to the tetragonal phase whose lattice parameters are $a = 0.3915 \text{ nm}$, $c = 0.8076 \text{ nm}$ (space group: P4/nmm, JCPDS card no. 73-2061). It was indicated that the BiOBr catalysts were synthesized successfully. Furthermore, the samples synthesized by 1-butyl-3-methylimidazolium bromide were also characterized by SEM, which were exhibited in Fig. 2. It can be seen from SEM images that BiOBr- C_4 with aggregated, tremella-ball-like structures were formed, which was similar to the BiOBr reported early [13]. The samples' surfaces were comprised of numerous layered-intercross BiOBr, which was different from the traditional layered BiOBr that synthesized by NaBr or KBr. This special morphology can make full use of the light, which might due to the multiple reflections among the layered-intercross appearance. From those results, the BiOBr samples have been successfully prepared by different kinds of the ILs, especially by 1-butyl-3-methylimidazolium bromide. In the procedure of the preparation, the ILs played not only the role of the bromide sources, but also the templates and the solvents of the fabrication of BiOBr, which exhibited the microflowers morphology.

UV–vis diffuse reflectance spectroscopy was conducted to measure the BiOBr samples' optical properties. The band gap energy (E_g) of BiOBr prepared with different kinds of ILs can be estimated according to the Eq. (1) and the diagram was exhibited in Fig. 3a and b.

$$ah\nu = k(h\nu - E_g)^{1/n} \quad (1)$$

where, k represents a constant, a , h , ν and E_g is absorption coefficient, Plank constant, light frequency, and band gap, respectively. By extrapolating the linear region, the band gap energies of BiOBr- C_4 , BiOBr- C_8 , BiOBr- C_{12} and BiOBr- C_{16} were calculated to be 2.31, 2.30, 2.27, 2.21 eV, respectively. Moreover, those as-prepared catalysts have proper band gaps to be activated

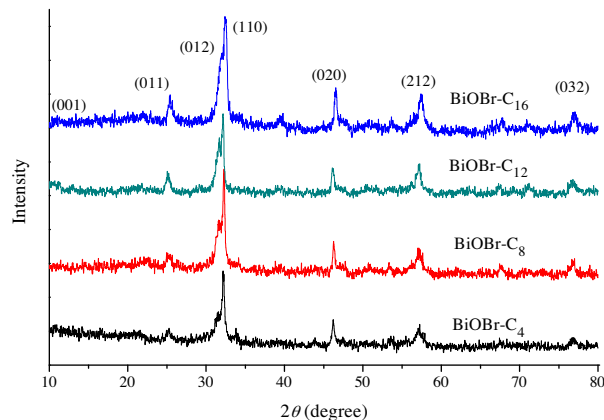


Fig. 1. XRD patterns for BiOBr samples prepared under different kinds of ionic liquids.

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