



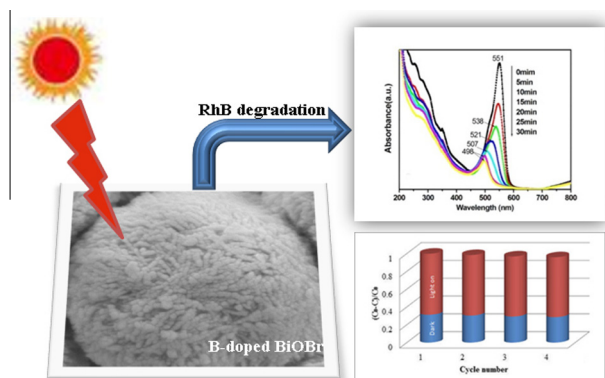
Boron-doped bismuth oxybromide microspheres with enhanced surface hydroxyl groups: Synthesis, characterization and dramatic photocatalytic activity



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GRAPHICAL ABSTRACT



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ABSTRACT

B-doped BiOBr photocatalysts were successfully synthesized via a facile solvothermal method with boric acid used as boron source. As-obtained products consist of novel hierarchical microspheres, whose nanosheet building units were formed by nanoparticles splicing. They showed dramatic photocatalytic efficiency toward the degradation of Rhodamine B (RhB) and phenol under the visible-light irradiation and the highest activity was achieved by 0.075B-BiOBr. The enhanced photocatalytic activity could be attributed to the enriched surface hydroxyl groups on B-doped BiOBr samples, which not only improved the adsorption of pollutant on the photocatalyst but also promoted the separation of photogenerated electron–hole pairs. In addition, it was found that the main reactive species responsible for the degradation of organic pollutant were h^+ and $\cdot O_2^-$ radicals, instead of $\cdot OH$ radicals.

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1. Introduction

Over the past decades, heterogeneous photocatalysis has attracted considerable attention in water treatment applications. It offers a way to eliminate organic pollutants from the wastewater

by using unlimited and green solar energy. TiO_2 is the most widely investigated photocatalyst due to its high photoactivity, low cost, low toxicity and good chemical stability [1,2]. However, TiO_2 only responds to solar ultraviolet irradiation because of wide band gap, and only less than 5% of the solar spectrum is exploited. Therefore, exploring new kinds of visible-light-driven photocatalysts has become one of the most hot research topics. So far, many visible light responsible photocatalysts, such as $AgPO_4$ [3], $BiVO_4$ [4,5],

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$\text{Bi}_{12}\text{TiO}_{20}$ [6], Bi_2WO_6 [7,8], BiOBr [9,10] and $g\text{-C}_3\text{N}_4$ [11], have been developed. Among them, BiOBr has been intensively investigated owing to its stability, suitable band gap and relatively superior photocatalytic ability [12,13].

As a p-type semiconductor, BiOBr belongs to a tetragonal PbFCl -type structure (space group $P4/nmm$; No. 129). It crystallizes in a layered structure, which consists of $[\text{Br}-\text{Bi}-\text{O}-\text{Bi}-\text{Br}]$ sheets stacked together by van der Waals forces along the c -axis. The strong intralayer bonding and the weak interlayer van der Waals interaction lead to highly anisotropic electrical and optical properties, which reduce the recombination probability of the photogenerated electrons and holes [14,15]. Previously, BiOBr has exhibited considerable visible-light photocatalytic performance in the degradation of organic contaminants [16,17]. However, it is still far from efficient for practical applications and needs some further improvements. In general, doping is an effective way to enhance the photocatalytic performance. Doping BiOBr with metals, such as Al [18], Ag [19], Fe [20] and Ti [21], has been reported to improve the charge separation, reduce the band gap energy and thus improve the photocatalytic activity. However, to the best of our knowledge, there have been limited reports on non-metal doped BiOBr so far [22]. Recently, elemental boron (B) has aroused wide interest because of its semiconducting property, and its use in photocatalysis (B-TiO_2 , $\text{B-Bi}_2\text{WO}_6$ and B-BiVO_4) has been examined [23–25]. B atoms can be located in the lattice oxygen positions to narrow the band gap due to the overlap of a p orbital on B with a p orbital on O [23], and they can also be located in interstitial positions to act as an electron trap, both of which favor the enhancement of the photocatalytic activity. In view of these, it is logical to anticipate that doping BiOBr with B will improve the photocatalytic performance of BiOBr .

In this work, a series of B-doped BiOBr photocatalysts were prepared by a facile solvothermal method. The as-prepared samples were characterized by XRD, SEM, XPS, FT-IR, Raman, BET, DRS, PL and photocurrent measurement. The photocatalytic activity was evaluated by the photodegradation of Rhodamine B (RhB) and phenol under visible light irradiation. The results show that B-doped BiOBr samples exhibit higher photocatalytic performance than pure BiOBr . The mechanism of the enhanced photocatalytic activity is discussed in detail.

2. Experimental

2.1. Sample preparation

All chemicals were used as received without further purification. The B-doped BiOBr photocatalysts were synthesized by a solvothermal method as follows: 0.97 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.73 g of cetyltriethylammonium bromide (CTAB) were orderly dissolved in 80 ml of ethylene glycol (EG), and then certain amount of boric acid (HBO_3) was added under magnetic stirring. After stirred for 30 min, the mixture was transferred into a 100 ml Teflon-lined autoclave. The autoclave was sealed and heated at 160°C for 16 h. After cooling down to room temperature naturally, the products were collected and repeatedly washed with absolute ethanol and distilled water, and then dried at 80°C . As-obtained samples were denoted as $x\text{B-BiOBr}$, where x represents the initial molar ratio of B to Bi (0, 0.025, 0.05, 0.075, and 0.1).

2.2. Characterization

The crystal structures and phase compositions of the samples were examined by X-ray diffraction (XRD, Bruker D8 Advance). The morphology was observed using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) equipped with an

energy dispersive X-ray spectrometer (EDS). The surface properties of the samples were examined by X-ray photoelectron spectroscopy (XPS: Thermo ESCALAB250, USA). FT-IR spectra were recorded by Vertex80 FTIR spectrometer. The Raman spectrum was obtained by a Bruker Senterra. Brunauer–Emmett–Teller (BET) surface area measurements were performed on a Quantachrome NOVA-4200E system. The optical property was analyzed by both UV–vis diffuse reflectance spectra (DRS, Varian Cary 300) and photoluminescence spectra (PL, Varian Cary-Eclipse 500).

2.3. Photocatalytic test

The photocatalytic performance of the samples was evaluated by the degradation of RhB and phenol under visible light irradiation. 0.1 g of photocatalyst was added into 100 mL of 15 mg/L RhB/phenol aqueous solution. A 150 W tungsten–halogen lamp (Beijing Institute of Opto-Electronic Technology) with a 420 nm cutoff filter was acted as a visible light source. Before irradiation, the suspension was stirred for 10 min in the dark to reach the adsorption–desorption equilibrium. At given irradiation time intervals, about 3 ml suspensions were taken and centrifuged to remove the catalyst particles. The concentration of remnant RhB/phenol was evaluated by the UV–vis spectroscopy at $\lambda = 553/270$ nm.

2.4. Photocurrent measurement

Transient photocurrent measurements were performed on a CHI660B electro-chemical workstation with a standard three-electrode configuration. A platinum plate was used as counter electrode, and Ag/AgCl electrode (saturated KCl) as the reference electrode. For preparation of working electrodes, 2 mg catalysts were suspended in 0.2 mL of ethanol and 0.2 mL of EG to produce slurry. 20 μL of the suspension was dropped on $1.5 \times 1.5 \text{ cm}^2$ fluorine-tin oxide (FTO) glass. The obtained film electrode was dried under ambient conditions. The electrolyte was 0.5M Na_2SO_4 aqueous solution. A 300 W Xenon lamp was utilized as the visible light irradiation source. The measurements were carried out at room temperature.

3. Results and discussion

3.1. Characterization

The phases and crystallinity of as-prepared samples was investigated by XRD. As shown in Fig. 1a, the diffraction peaks of all the samples can match the standard tetragonal BiOBr phase (JCPDS 09-0393), and no impurity phase can be observed, indicating that B dopant does not change the phase structure. However, it is worth noting that the positions of (012) and (110) peak shift gradually to a higher angle with the increase of the B content (Fig. 1b). According to Bragg's law, the increase in the 2θ value means the decrease of the crystalline lattice parameters. In general, there are two doping modes for B dopant, i.e. interstitial mode and substitutional mode. The former will make the lattice parameters to increase, while the latter can cause an uncertain change in the lattice parameters, which depends on the differences of the ionic radius. Considered that the ionic radius of B^{3+} ions (23 pm) is much smaller than that of Bi^{3+} (96 pm), the shift of diffraction peaks may suggest that boron ions are doped into BiOBr lattice by substituting Bi^{3+} ions.

The surface composition and chemical states of the elements were characterized by XPS. Fig. 2a–d shows high-resolution XPS spectra of the primary elements. In Fig. 2a, two strong symmetrical peaks centered at 159.8 and 165.1 eV can be observed in pure

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