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BiOBr photocatalysts with tunable exposing proportion of {001} facets: Combustion synthesis, characterization, and high visible-light photocatalytic properties

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ABSTRACT

BiOBr photocatalysts were synthesized by the combustion method. The BiOBr nanosheets possessing pure tetragonal BiOBr phase with high ratio of {001} facets exposure were obtained. The thickness of BiOBr nanosheets, in other words, the exposing proportion of {001} facets can be modulated through changing the added amount of ammonium bromide. The band gap energy of BiOBr was increased with larger exposing proportion of {001} facets. BiOBr with the thinest sheets exhibited the best photocatalytic activity of Rhodamine B under visible-light irradiation. To the end, the corresponding plausible growth mechanism of BiOBr was presented.

1. Introduction

Over the past few years, photocatalysis has attracted much attention due to its potential application in decomposing organic compounds for environmental remediation [1–3]. Several photocatalytic semiconductor materials, such as TiO_2 and ZnO, have been widely used, but they have the limitation that they can only absorb ultraviolet light, which accounts for just a tiny portion of the sunlight [4–8]. In recent years, bismuth oxybromide (BiOBr) has received much attention due to its potential photocatalytic abilities under visible light [9]. BiOBr is of tetragonal structure that consists of tetragonal $[Bi_2O_2]$ positively charged slabs, which are interleaved by double slabs of bromine atoms to form [Br–Bi–O–Bi–Br] layers along the *c*-axis [10]. The self-built electric field between $[Bi_2O_2]$ and Br slabs would effectively separate the photoinduced electron–hole pairs, thus transfer the electrons and holes to the surface of BiOBr, which would enhance the photocatalytic activity [11]. Up to now, various BiOBr micro/nano-structures, including nanoparticles, nanotubes and nanobelts, nanoplates, and microsheets, have been successfully fabricated by means of the microemulsion, solvothermal, and sol–gel methods. For instance, Xiong has demonstrated for the first time the direct conversion of metallic Bi nanospheres into three-dimensional (3D) flower-like BiOBr nanoarchitectures at room temperature [10]. Xu and co-workers successfully prepared two-dimensional and three-dimensional BiOBr via the facile co-precipitation methods with $Bi(NO_3)_3 \cdot 5H_2O$ as the Bi source [12]. BiOBr photocatalysts with various morphologies have been synthesized via the solvothermal method in ethanol-, ethylene glycol- and glycerol-mediated conditions, respectively [13]. Shang has proposed the hydrothermal method for visible-light-induced photocatalyst BiOBr, in which cetyltrimethylammonium bromide (CTAB) acted as not only the template but also the Br source [14]. Moreover, Cheng has demonstrated a one-pot miniemulsion synthesis of BiOBr hollow microspheres [15].

Previous studies have proposed that {001} facets are the active photocatalysis facets in BiOBr crystals [3,9], thus high exposing proportion of {001} facets should be beneficial to improved photoactivity of BiOBr. Herein, for the first time, we report a facile and rapid combustion method to synthesize BiOBr nanosheets with tunable exposing proportion of {001} facets via a simple one-step combustion method at ~300 °C. Of particular interest is that the thickness of BiOBr sheets, in other words, the exposed ratio of {001} facets can be modulated through varying the added amount of ammonium bromide, leading to different photocatalytic performances of as-synthesized BiOBr.

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2. Experimental

All the chemical reagents of analytical grade were purchased from Aladdin Industrial Corporation and used without further purification. Deionized water was used throughout the work. BiOBr photocatalysts were synthesized by the combustion method. First, 0.02 mol bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) was dissolved in 20 mL deionized water, followed by the addition of 4 mL concentrated nitric acid (65%) under vigorous stirring to obtain a transparent solution. In addition, bromide ammonium (NH_4Br) with different molar ratios of $NH_4Br/Bi(NO_3)_3 \cdot 5H_2O$ (3, 4, and 5) and 0.04 mol urea were added to 20 mL deionized water. The obtained solution was added quickly into the above $Bi(NO_3)_3$ solution. Then, the beaker containing reaction mixture was transferred to an electric jacket at a temperature of 300 °C in air and the solvent was thus removed. Finally, combustion reaction took place due to the exothermic redox reaction of nitrates and urea [16]. All BiOBr samples were labeled as BiOBr-molar ratio of $NH_4Br/Bi(NO_3)_3$.

Photocatalysis experiment was carried out in a home-made photocatalytic reaction box. A 300 W Xenon lamp with a UV cutoff filter (JB450) was positioned about 10 cm over a cylindrical container with a circulating water jacket for cooling. BiOBr (100 mg) was dispersed in 100 mL aqueous solution of rhodamine B (RhB) (20 mg/L). The solution was stirred in dark for 30 min to ensure the establishment of the adsorption–desorption equilibrium. The concentration of RhB was analyzed by recording the absorption band maximum (554 nm) in the absorption spectra and taken as the initial concentration (C_0). During the irradiation, 5 mL solution was extracted at an interval of 10 min, then absorbance of RhB solution was measured after centrifugation at 1000 rpm for 5 min to remove the catalysts. The normalized temporal concentration changes (C/C_0) of RhB were obtained.

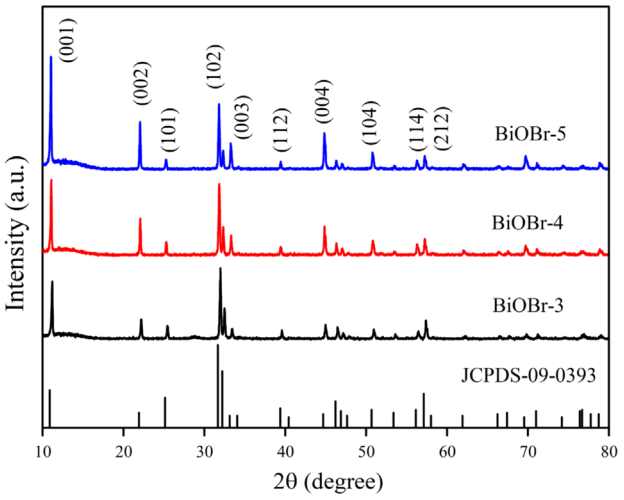

Fig. 1. XRD patterns of BiOBr samples.

3. Results and discussion

Fig. 1 shows the XRD patterns of samples. All patterns are indexed as pure phase of BiOBr (JCPDS Card no. 09-0393) and no other peaks for impurities are detected. The relative diffraction intensities of peaks with {001} facets are distinctly much stronger than that of standard PDF card [14], indicating BiOBr anisotropic growth along the {001} plane, due to the high thermodynamic stability of the {001} facets [11]. Moreover, the relative diffraction intensity of the {001} peak became stronger with increasing added amount of NH_4Br, suggesting the higher exposing proportion of {001} facets.

The morphologies and structures of the samples were characterized by SEM and TEM, as shown in Fig. 2. All samples exhibit flaky morphology with the in-plane size of 1–8 μm. As shown in

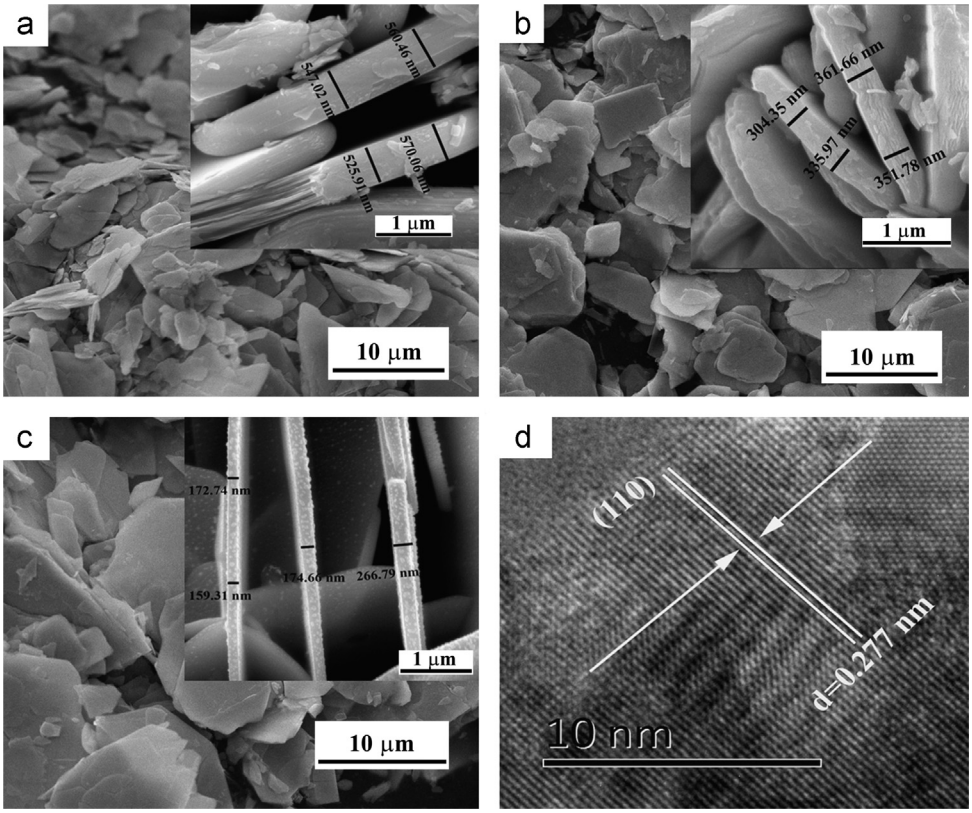

Fig. 2. SEM images of (a) BiOBr-3, (b) −4, (c) −5; (d) TEM image of BiOBr-5.