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Solvothermal synthesis and photocatalytic activity of Al-doped BiOBr microspheres

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Abstract

A series of Al-doped BiOBr microspheres with different Al contents were synthesized via a facile solvothermal method. The as-prepared samples were characterized by X-ray diffraction(XRD), scanning electron microscopy(SEM), energy dispersive spectrometry(EDS), X-ray photoelectron spectroscopy(XPS), N_2 adsorption–desorption and UV–visible diffuse reflectance spectroscopy(UV–vis DRS). The photocatalytic activity was evaluated by the photocatalytic degradation of methyl orange in an aqueous solution under visible light irradiation. The results revealed that Al doping could greatly improve photocatalytic performance of BiOBr and different Al contents resulted in different photocatalytic activities. The highest activity was achieved by 4 at%Al-BiOBr. The enhanced photocatalytic activity was attributed to efficient separation of photogenerated electron–hole pairs and large BET surface area.

Keywords: Chemical preparation; Mesoporous microsphere; BiOBr; Photocatalytic property

1. Introduction

Semiconductor photocatalysts have received considerable attention due to their applications in decomposing organic compounds for environmental remediation. Among photocatalysts, TiO_2 has been mostly developed owing to its cheapness, strong oxidizing power and nontoxicit [1]. However, due to its wide band gap (~3.2 eV), only a small fraction of solar energy can be effectively absorbed and used for photodegradation processes [2]. Therefore, in order to improve the utilization of solar energy in photocatalytic processes, the development of a visible light photocatalyst has become an imperative topic in current photocatalysis research.

In recent years, BiOBr has attracted considerable attention owing to its potential photocatalysis application [3,4]. BiOBr is a lamellar-structured p-type semiconductor with intrinsic indirect band gap. The lamellar structure is composed of $[Bi_2O_2]^{2+}$ layers interleaved with double Br layers, which endows BiOBr with unique electrical, optical and catalytic activity [5]. Nonetheless, the band gap of BiOBr was reported to be in the range of 2.8–2.9 eV [6], indicating that it could only absorb a part of the visible light. In order to utilize visible light more efficiently and enhance visible light photocatalytic activity of BiOBr, intensive research efforts have focused on two major strategies. One is to combine BiOBr with other semiconductors/noble metals to form heterojunctions, such as $ZnFe_2O_4$/BiOBr and Ag/BiOBr [7,8], which have been reported to be more flexible for broadening the visible light absorption and less sensitive to the component homogeneity. The other is to fabricate BiOBr-based solid solutions such as $BiOCl_{1-x}Br_x$ and $BiOI_{1-x}Br_x$ [9,10], which are believed to possess tunable optical band gaps and exhibit high photocatalytic activities under visible light irradiation. In addition, metal ions doping may also be an effective way to improve the photocatalytic activity. Doping BiOBr with transition metals, such as Ti [11,12] and Fe [13], has been reported to extend the wavelength response range towards the visible region, thus result in the enhanced photocatalytic activity. However, to the best of our knowledge, there have been no reports of non-transition-metal doped BiOBr so

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far. Recent studies show that Al is a better dopant in photocatalysts [14–16]. Therefore, it is expected that Al doping will improve the photocatalytic performance of BiOBr.

In this paper, a series of Al-doped BiOBr microspheres with different Al contents were prepared by a simple solvothermal method. The as-obtained samples were characterized by XRD, SEM, EDS, XPS, N_2 adsorption–desorption and UV–vis DRS. The photocatalytic activity was studied by the photocatalytic degradation of methyl orange under visible light irradiation. The influence of Al doping on the photocatalytic activity of BiOBr was investigated and discussed.

2. Experimental

2.1. Sample preparation

All chemicals were analytical grade and used as received without further purification. Al-doped BiOBr photocatalysts were synthesized by a facile solvothermal method. First, a total of 1 mmol of stoichiometric $Bi(NO_3)_3 \cdot 5H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved into 20 ml of ethylene glycol (EG), in which Al contents were 1, 2, 4 and 6 at%, respectively. Then, another 20 ml of EG solution containing 1 mmol of cetyltriethylammnonium bromide (CTAB) was dropped into the above solution. The resultant precursor solution was poured into a 50 ml Teflon-lined autoclave after 30 min of stirring. Finally, the autoclave was kept at 160 °C for 8 h and allowed to cool down to room temperature naturally. The precipitate was washed with absolute ethanol and distilled water for three times, respectively, and dried at 80 °C in air. The as-obtained samples were named as *x*%Al-BiOBr, where *x* represents the Al content.

2.2. Characterization

The phase structure of the as-prepared samples was characterized by X-ray diffractometer (XRD, Bruker D8 Advance with CuKa1 radiation at 40 kV and 30 mA). The surface properties of the samples were examined by X-ray photoelectron spectroscopy (XPS) with Al *K*α X-rays ($h\nu$=1486.6 eV) irradiation operating at 150 W (XPS: Thermo ESCALAB250, USA). The morphological investigation was carried out by a scanning electron microscopy (SEM, FEI Quanta-250) equipped with an energy dispersive X-ray spectrometer (EDS). The Brunauer–Emmett–Teller (BET) surface area was determined by N_2 adsorption–desorption isotherm measurement at 77 K on a Quantachrome NOVA-4200E system. The optical property was analyzed by UV–vis diffuse reflectance spectra (DRS, Varian Cary 300).

2.3. Photocatalytic test

The photocatalytic activity of the samples was determined by the photocatalytic degradation of methyl orange(MO) in an aqueous solution under visible light irradiation. The visible light source was a 150 W tungsten–halogen lamp (Beijing Institute of Opto-Electronic Technology, light intensity=200 mW/cm^2). The experiments were carried out at 25 ± 3 °C as follows: 0.1 g of photocatalyst was added into 100 ml of 10 mg/l MO solution. The distance between the bottom of the lamp and the top of the solution was 20 cm. Before irradiation, the suspension was stirred in dark for 30 min to ensure the establishment of adsorption–desorption equilibrium. At given irradiation time intervals, 3 ml of suspension was taken and centrifuged to remove the catalyst particles. The concentration of MO was determined by the UV–vis spectrophotometer.

3. Results and discussion

3.1. Characterization

3.1.1. XRD patterns

The XRD patterns of pure BiOBr and Al-doped BiOBr samples are depicted in Fig. 1a. All the diffraction peaks can be readily indexed to a pure tetragonal phase BiOBr based on the data files (JCPDS card no. 73–2061). No other diffraction peaks are observed, indicating that Al doping does not alter the crystal structure of BiOBr. However, it is worth noting that the position of (1 1 0) peak undergoes a gradual shift toward

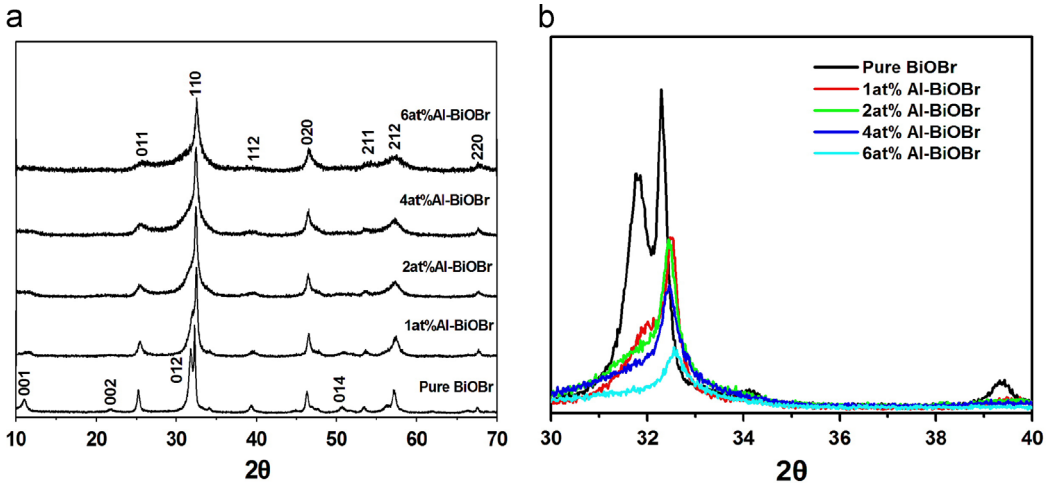

Fig. 1. XRD patterns of pure BiOBr and Al-doped BiOBr samples.