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Simultaneously promoting charge separation and photoabsorption of BiOX (X = Cl, Br) for efficient visible-light photocatalysis and photosensitization by compositing low-cost biochar

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ABSTRACT

Exploration of novel and efficient composite photocatalysts is of great significance for advancing the practical application of photocatalysis. BiOX (X = Cl, Br) is a kind of promising photocatalysts, but the charge separation efficiency and photoabsorption need to be ameliorated. In this work, we first employ a low-cost and easily accessable carbon material biochar to modify BiOX (X = Cl, Br) and develop biochar/BiOX (X = Cl, Br) composite photocatalysts via a facile *in-situ* deposition method. The as-prepared composites are detailedly characterized by SEM, SEM-mapping, TEM, XRD and XPS, and DRS result demonstrates that the visible-light absorption of BiOX (X = Cl, Br) catalysts can be exceedingly enhanced by biochar. The biochar/BiOX (X = Cl, Br) composites are found to unfold remarkably enhanced visible-light-driven photocatalytic activity toward degradation of MO and photocurrent generation. The strengthened photocatalytic performance mainly stems from the profoundly improved charge separation and delivery efficiency, as evidenced by the electrochemical impedance spectra (EIS), photoluminescence (PL), and time-resolved PL decay spectra. Additionally, the biochar exerts importance in enhancing the two different types of photochemical reactions of BiOBr and BiOCl, in which the photocatalytic mechanisms are found to be photocatalysis and photosensitization process, respectively. The present work may open up a new avenue for framing economic and efficient photocatalytic materials and new composite materials for photoelectric application.

1. Introduction

With the reduction of the fossil fuel and the destruction of the environment, development and using clean and renewable resources become an urgent problem. The photocatalytic technology, which makes use of solar to degrade organic pollutants, produce hydrogen by water splitting and convert CO_2 to new energy, has generated widespread research interest [1–3].

BiOX (X = Cl, Br, I) is a kind of excellent semiconductor photocatalytic material with multiple advantages, such as high catalytic activity, good stability, simple preparation process, low environmental toxicity, and so on [4]. The excellent performance of BiOX (X = Cl, Br, I) is mainly originated from their layered structure, which is composed of $[Bi_2O_2]$ slabs interleaved with double halogen atom slabs [5]. The special internal electric field between bismuth oxide layer and halogen atom can effectively separate electrons and holes, thus enabling BiOX materials to show extensive applications in degrading dyes [6–8], kinds of phenolic [9,10], water pollutant [11] and many antibiotics [12], etc. In recent years, some new applications of BiOX (X = Cl, Br, I) were also discovered. For example, Wu et al. found that BiOCl colloidal ultrathin nanosheets showed high catalytic activity and excellent selectivity toward the aerobic oxidation of secondary amines to imines [13]. Li et al. synthesized BiOBr nanosheets with oxygen vacancies on the exposed {001} facets and first used them for nitrogen fixation in which N_2 in atmospheric can be reduced to NH_3 efficiently [14]. However, the separation

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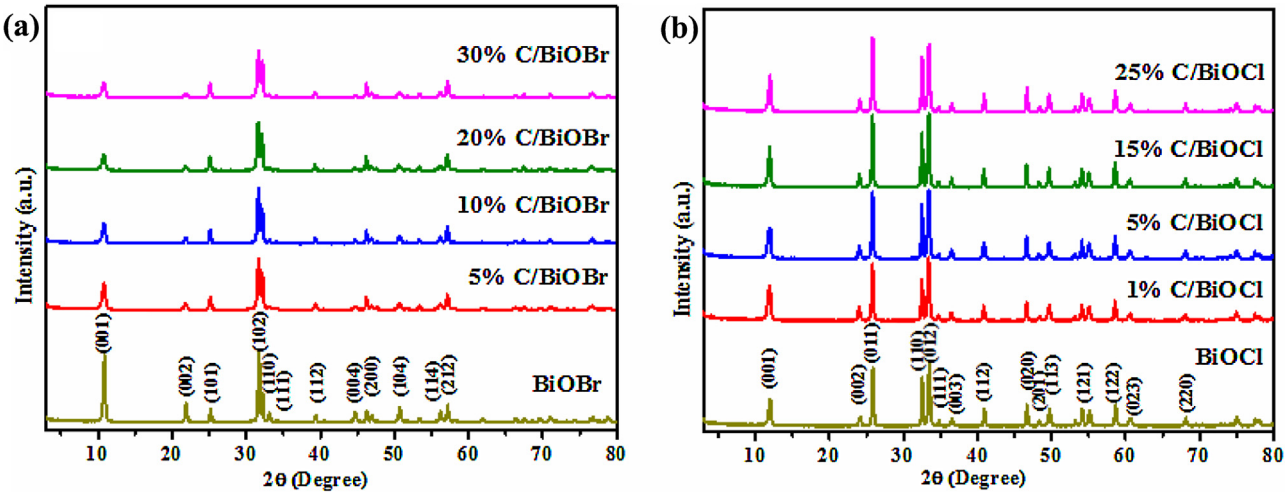

Fig 1. XRD patterns of the pure BiOX and C/BiOX photocatalysts.

efficiency of photogenerated electrons and holes of BiOX needs to be further improved to meet the practical requirement. On the other hand, the inherent large band gaps of BiOCl (~3.4 eV) and BiOBr (~2.6 eV) pre-eminently restricted their applications in solar conversion [15,16]. As a result, the study on the charge separation efficiency and enhancement of visible light absorption of is of great significance and necessity for the practical applications of BiOCl and BiOBr.

Constructing composite materials is an effective way to improve the separation efficiency of photogenrated electron-hole pairs of photocatalysts. Many BiOX (X = Cl, Br) based composite materials have been designed by combining with Ag [17,18], C_3N_4 [19–21], CdS [22], $BiVO_4$ [23], $BiPO_4$ [24–26] and Bi_2WO_6 [27], carbon quantum dots [28], bismuth oxyhydrate [29] or forming solid solution [30–32]. Especially, the carbon materials, such as graphene [33,34], carbon nanotube [35], etc, have been reported to promote the charge separation and enables BiOX an enhanced photocatalytic activity. Biochar is a porous carbon-residue derived from the thermal conversion of waste biomass under limited oxygen or anaerobic conditions. To date, there has been a growing body of literature on the application of biochar in water treatment. It has been reported that the conductive carbon materials can serve as efficient electron-transfer channels and acceptors to improve the separation of photogenerated electron–hole pairs [36,37]. However, these carbon materials suffer from many drawbacks, such as high cost, complex synthesis procedure, etc. Therefore, developing novel carbon materials to improve the optical and photocatalytic properties of BiOX is desirable and tempting.

Herein, we for the first time utilize biochar, a low-cost and easily accessable carbon material, to fabricate C/BiOX (X = Cl, Br) composite photocatalysts by depositing simply BiOX nanosheets on the surface of biochar. The structure, microstructure and photoabsorption of as-prepared samples are systematically investigated by multiple techniques. The C/BiOX (X = Cl, Br) show obvious enhancement on photochemical and photoelectrochemical properties compared to the pure BiOBr and BiOCl under visible light (λ > 420 nm). The fine characterizations on charge movement disclose that the facilitated separation and transfer of charge carriers account for the improved properties. In addition, the different photochemical-reaction mechanisms for enhanced photoreactivities of BiOBr and BiOCl in composites are studied and proposed.

2. Experimental

2.1. Preparation of C/BiOX (X = Br, Cl)

The C/BiOX powders were synthesized by a one-step hydrolysis method. The biochar was obtained from Yineng Co., Ltd. in Shandong province, China. All of the reagents used in the experiment were analytical grade. Typically, 2 mmol $Bi(NO_3)_3{\cdot}5H_2O$ was completely dispersed in 20 mL ethylene glycol at room temperature. After that, different masses of biochar (different mass ratios with BiOX) were dispersed evenly in 20 mL distilled water by ultrasonic treatment, and then the suspensions were dropped into the $Bi(NO_3)_3{\cdot}5H_2O$ solution. Next, 2 mmol KX (X = Br, Cl) was dissolved uniformly in 20 mL distilled water, and then dropped to the mixed solution slowly. The mixed solution was stirred at room temperature for 12 h. Afterwards, the products were collected and washed with ethanol and deionized water for 3 times and dried at 60 °C. The samples were marked as BiOBr, 5% C/BiOBr, 10% C/BiOBr, 20% C/BiOBr, 30% C/BiOBr, BiOCl, 1% C/BiOCl, 5% C/BiOCl, 15% C/BiOCl and 25% C/BiOCl, respectively.

2.2. Characterization

The phase structure of different samples was analyzed with the X-ray diffractometer (D/MAX-RC, Rigaku, Japan) using CuKα radiation (40 kV, 100 mA). All XRD patterns were obtained from 3° to 80° with a scan speed of 8°/min. The microstructure and morphology of the photocatalysts were researched by scanning electron microscopy (SEM, S-4800 Hitachi, Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were detected by a JEM-2001 F electron microscopy (JEOL, Japan). The surface properties of the as-synthesized samples were performed by the X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi ThermoFisher, UK). The optical properties were measured by the UV–vis diffuse reflectance spectra (DRS) using a UV–vis spectrophotometer (Varian Cary 5000, USA). The fluorescence decay spectrum was measured by the fluorescence decay spectrometer (HORIBA, JOBIN YVON FL3-21) and 370 nm pulse laser radiation (nano-LED) was used as the excitation source with the pulse width of the laser 12 ns. The photoluminescence excitation (PLE) and emission (PL) were investigated by a fluorescence spectrophotometer (F-4600 Hitachi, Japan) with a