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Synthesis and photocatalytic activity of BiOBr nanosheets with tunable exposed {0 1 0} facets

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ABSTRACT

A series of BiOBr nanosheets with tunable exposing proportion of (0 1 0) facets had been synthesized. In the synthesis process, different *n*-alcohols are used, which not only promote the exposure of (0 1 0) facets, but also modulate the size and thickness of these BiOBr nanosheets in a wide range. Furthermore, these nanosheets showed an efficient photodegradation activity for salicylic acid (SA) and Rhodamine B (RhB). By comparison, the sample prepared in *n*-hexanol possessed the highest photocatalytic activity than those synthesized in *n*-butanol and methanol, respectively. This excellent photocatalytic activity was attributed to the thin lamellar thickness and the exposure of (0 1 0) facets, which facilitated the separation of photoinduced electrons and holes.

1. Introduction

With the consumption of fossil fuels in the past centuries, human beings are now faced with great energy crisis and environmental issues. Semiconductor photocatalysis, which could use the clean and abundant solar energy for pollutant decomposition [1], water splitting [2] and CO_2 conversion [3], has been regarded as a green and promising alternative solution to energy substitution and environmental management. Rencently, Bismuth oxyhalides (BiOX (X = F, Cl, Br, I)), especially BiOBr, had attracted considerable interests. BiOBr is a novel *p*-type semiconductor crystallized in a tetragonal matlockite structure with $[Bi_2O_2]^{2+}$ slabs interleaved by double slabs of Br ions [4]. Compared with traditional photocatalysts such as TiO_2, BiOBr materials possess wider visible-light response range, better electrical conductivity and higher quantum efficiency [5,6]. Therefore, it possesses wide applications in heavy metal removal [7], nitrogen fixation [8] and sterilization [9]. However, despite the wide use of BiOBr materials in the laboratory, the narrow range of visible-light response and the inefficient charge separation and transportation restrict its use in industrial fields [10]. Therefore, modification methods were needed to enhance the photocatalytic activity of BiOBr.

Up to date, various methods had been used, such as hierarchical nanostructures [11–13], halogen-mixing solid solutions [14] and crystal-facet control [15]. Among them, the facets-controlled synthesis of BiOBr is worthy to be mentioned, especially synthesizing crystals with tunable exposed facets. In the past few years, BiOBr nanosheets with tunable exposed (0 0 1) facets were prepared [16]. Generally, the intra-electric field of BiOBr materials is along the [0 0 1] direction and the surface energy of (0 0 1) facets is much lower than other facets [17]. Therefore, BiOBr nanosheets with dominant exposed (0 0 1) facets possess higher photocatalytic activity and are easily prepared. Contrast to the (0 0 1) faces of BiOBr materials, the (0 1 0) facets were also of vital importance [18]. In general, (0 1 0) facets had open channel characteristics, which benefiting the injection of photoinduced electrons from dyes and possessing superior activity for indirect dye sensitization degradation under visible light [19]. However, BiOBr materials with dominant exposed (0 1 0) facets were hard to obtained due to the high surface energy [20]. Therefore, special preparation methods were needed. In previous reports, BiOBr nanosheets with dominant exposed (0 1 0) facets were synthesized by adding NaOH solution [21]. However, this synthetic method has its limitations: Adding NaOH solution will lead to a complicated synthetic process, if adding more NaOH in the preparation system, a dehalogenation effect may occur and the chemical compositions will change [22]. Particularly, changing the proportion of exposed (0 1 0) facets seems hard with this method. To the best of our knowledge, there is no report on the design and fabrication of BiOBr nanosheets with tunable exposured (0 1 0) facets just by changing the solvents.

Herein, in this study, we used a novel method to synthesize BiOBr nanosheets with tunable exposed (0 1 0) facets. The facet-

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dependent photocatalytic activities of the as-obtained nanosheets are studied through the degradation of salicylic acid (SA) and Rhodamine B (RhB) under visible-light. To understand the excellent photocatalytic activity of the BiOBr materials, several factors such as morphology, specific surface area and electron transport have been studied. The thinnest nanosheets with the highest exposure ratio of (0 1 0) facets possessed the highest photocatalytic activity. Considering that the morphology and crystal facets impacted the performance of these BiOBr nanosheets, the role of solvents in the synthetic process was systematically investigated by calculation and theoretical prediction. Therefore, a “solvent-dependent” study had been used to investigate the controllable synthesis of BiOBr nanosheets and the growth of BiOBr crystals. This work provided a novel method for synthesizing photocatalysts with highly efficient photocatalytic performance.

2. Materials and methods

2.1. Materials

Bismuth nitrate pentahydrate [$Bi(NO_3)_3·5H_2O$], acetic acid, NaBr and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, P. R. China). *n*-butanol, *n*-hexanol and *n*-hexyl acetate were purchased from Aladdin (Shanghai, China). All of the reagents were analytical grade and used without further purification.

2.2. Sample preparation

In a typical process, 1 mmol of $Bi(NO_3)_3·5H_2O$ was dissolved into 3 mL of acetic acid and labeled as solution A. Mean while, 1 mmol of NaBr was added into 30 mL of *n*-alcohol (methanol, *n*-butanol and *n*-hexanol, respectively), and labeled as solution B. The mixture were stirred and sonicated until all of the chemicals were well dispersed. Subsequently, solution B was slowly added to solution A in drops with continuous stirring and sonicating, and a white precipitate was formed during this process. Then, the mixed solution was transferred to a stainless steel vessel, which was subsequently heated to 180 °C and maintained at the temperature for 5 h. When cooling down to room temperature naturally, the obtained product was collected and washed with deionized water and ethanol several times, and finally dried in the air for further use. BiOBr samples were labeled as BiOBr (M), BiOBr (B), BiOBr (H), corresponding to the different solvent methanol, *n*-butanol and *n*-hexanol, respectively. For comparison, the sample prepared in absence of *n*-alcohol in solution B was referred to BiOBr (W).

2.3. Characterization

X-ray diffraction (XRD) patterns were carried out in a parallel mode ($\omega = 0.5^\circ$, 2θ varied from 20° to 80°) using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å).

The microstructure and composition size of the samples were investigated by a SU8000 field-emission scanning electron microscope (FESEM, Hitachi, Japan) at an accelerating voltage (3–5 KV), energy dispersive spectrum (EDS) was connected to the SEM. Transmission electron microscope (TEM) and high resolution transmission electron microscopy (HRTEM) were obtained on a Tecnai G20 (FEI Co., Holland) microscope operated at an accelerating voltage of 200 kV, the sample powder was dispersed into ethanol and dropped a very dilute suspension onto a copper grid. The UV–vis diffuse reflectance spectra (UV–vis DRS) were collected with a Shimadzu UV-2550 spectrophotometer from 200 to 800 nm using $BaSO_4$ as background. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer using Al Kα radiation as the excitation source. The Brunauer–Emmett–Teller (BET) specific surface areas of the samples were evaluated through the nitrogen adsorption and desorption isotherms using a Micromeritics ASAP 2020 gas adsorption apparatus (USA). Photoluminescence (PL) measurements were carried out at room temperature in a Hitachi F-7000 with a 150 W Xe lamp. The samples were excited at 300 nm, and the emission filter (300–800 nm) was used to minimize the background single at the excitation wavelength. The surface photovoltage (SPV) spectra measurement was carried out based on the lock-in amplifier. The measurement system consisted of a source of monochromatic light, a lock-in amplifier (SR830, Stanford Research Systems, Inc.) with a light chopper (SR540, Stanford Research Systems, Inc.), and a sample chamber. Salicylic acid (SA) and Rhodamine B (RhB) were chosen as the simulated pollutants to evaluate the photocatalytic activity of the as-prepared single crystalline nanosheets. The esters species after reaction were detected by an Alliance 2695 high performance liquid chromatography (HPLC) equipped with UV–vis diode array detector using a C18 inversed-phase column (Agilent Eclipse XDB-C18, 150 × 4.6 mm, 5 μm). Ultrapure water and methanol were used as mobile phase, the injection volumn was 10 μL and the flow rate was 1.0 mL min^{-1}.

2.4. Measurements of photocatalytic activity

The photocatalytic activity of the as-synthesized BiOBr samples was measured by the degradation of SA and RhB aqueous solution. A 350 W Xe lamp with an ultraviolet cutoff filter ($\lambda \geqq 420$ nm) was used to provide visible light. All experiments were carried out at 20 °C in an 80 mL of self-designed quartz photo-chemical reactor. The distance between the lamp and the glass reactor was about 5 cm. In each run, 50.0 mg catalyst was dispersed into 50.0 mL of RhB (20.0 mg L^{-1}) or SA (20.0 mg L^{-1}) aqueous solution. Then, the suspension was treated by ultrasonication for 10 min and stirred in dark for 1 h to ensure the establishment of the adsorption-desorption equilibrium. During the photoreaction, 5 mL of suspension was removed from the reactor at regular time intervals of 4 min and centrifuged. Finally, the concentration of catalyst-free RhB and SA solution were analyzed by the UV–vis spectrophotometer (UV-2550, Shimadzu). The active species during the photodegradation reaction were determined by dissolving 0.05 mmol trapping agents, including EDTA, $AgNO_3$, isopropanol (IPA), benzoquinone (BQ), which could capture photo-induced holes, photo-induced electrons, $^{\bullet}OH$ radical and $^{\bullet}O_2{}^{-}$ radical, respectively.

2.5. Theoretical calculation

The calculation for Bi^{3+} ions with CH_3COO—, CH_3 —O—, CH_3-$(CH_2)_3$ —O—, CH_3—$(CH_2)_5$ —O— and H^+ ions with acetic acid and terminated oxygen on the (0 0 1) surface were performed by density functional theory (DFT) method with B3LYP, which accompanied with basis sets of a 6–31 + G(d,p) set for H, O, C atoms and a lanl2dz set for Bi atom within the Gaussian 09 package. The $H^+ \longleftarrow HOOCCH_3$ and $H^+ \longleftarrow$ O–Bi system were optimized without any constraint in the beginning. The calculation for the H^+ systems took two forms: (I) the acetic acid coordinated to the H^+ atoms via the oxygen atom of the carbonyl ($H^+ \longleftarrow O{=}C$), (II) We had optimized the structure of (0 0 1) facets coordinating with H^+ and we found the binding energy of $H^+ \longleftarrow$ O—Bi was the lowest. In other words, H^+ preferred connecting with the oxygen atom of Bi-O bond during the synthetic process, thus we chose the oxygen atom of a single Bi-O bond to represent the terminated oxygen on (0 0 1) surface approximately.