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One-pot synthesis of Cu-doped bismuth oxychlorides single-crystal nanosheets with a high percentage of exposed {001} facets

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ABSTRACT

Facile synthesis of two-dimensional (2D) structured BiOCl is quite a challenge and a proven practicable solution to achieve superior photocatalytic property. One-pot synthesis of BiOCl single-crystal nanosheets with exposed {001} facets was achieved using a Cu-containing organic solvent. The Cu^{2+} ion or Cu_2O played an important role in controlling the shape and size of BiOCl nanosheets. Furthermore, EDX element mapping confirmed the presence of Cu-doping of the as-prepared BiOCl nanosheets.

1. Introduction

Bismuth oxychlorides (BiOCl), which is one of the multicomponent semiconductors, has attracted much attention due to its outstanding photocatalytic properties [1,2]. For single-crystalline BiOCl, the surface properties are vital to its physical and chemical performances. The different facets generally possessing different geometric and electronic structures endow single-crystalline materials with diverse properties [3–5]. For high-efficient photocatalysis, the effective adsorption of reactant molecules or ions should occur on the surface of photocatalysts. Different facets with unlike surface atomic structures could exhibit distinct abilities in adsorption capability [6,7]. Tailored synthesis of inorganic crystals with well-defined surfaces has attracted great attention due to facet-dependent photocatalytic, photoelectric and other surface-interrelated activities [8].

BiOCl single-crystalline nanosheets with exposed {001} facets exhibit high activities for direct semiconductor photoexcitation degradation of pollutants under UV irradiation [1]. The exposed {001} facets of BiOCl terminated with a high density of oxygen atoms are not only favorable for the adsorption of cationic dye, but also accumulate photogenerated electrons injected from the excited dye due to the internal electric field along [001] direction caused by $[Bi_2O_2]^{2+}$ layers and Cl atom layers [9,10]. Thus, the effective synthesis of BiOCl with a high area ratio of {001} reactive facet is highly desirable [11,12]. Li et al. reported that the thickness of BiOCl nanosheets along the [001] direction could be decreased from ~100 nm to ~30 nm by increasing the pH of the aqueous solution from 1 to 6, which could achieve a high area ratio of {001} facets [13]. BiOCl nanodisks with exposed {001} facets were synthesized by using water as the hydrolysis agent and ethylene glycol as the crystal growth inhibitor agent and the size and shape of BiOCl nanostructures could be effectively tuned through adjusting the volume ratio of ethylene glycol/H_2O [14]. The Fe(III) modified BiOCl ultrathin nanosheets with the exposure of active {001} facets have produced via a facile solvothermal approach by using the mannitol solution as the solvent and $FeCl_2$ as Fe source [15].

On the other hand, BiOCl is a wide band gap semiconductor, which makes only the ultraviolet radiation available and thus causes poor photocatalytic performance under visible light [16,17]. In order to expand the photon-response region to visible-light, doping is employed to engineer its band structure [18,19]. Copper (Cu) is one of the promising candidates which could be doped into BiOCl. Di et al. had successfully synthesized Cu-modified sphere-like BiOCl [20]. It is confirmed that the introduction of Cu elements brings a broad light absorption band to BiOCl, which enhances the photocurrent and photocatalytic activities.

In this work, BiOCl nanosheets with exposed {001} facets were synthesized by using a Cu-containing organic solvent. The controlled experiment was carried out to investigate the formation mechanisms of BiOCl nanosheets. During the one-pot solvothermal process of BiOCl nanosheets, CuO_2 cubes were synthesized simultaneously, which may play an important role in controlling the size and shape of BiOCl nanosheets as templates. Furthermore, Cu doping was detected in BiOCl nanosheets. To the best of our knowledge, Cu-doped BiOCl nanosheets with exposed {001} facets have never been reported.

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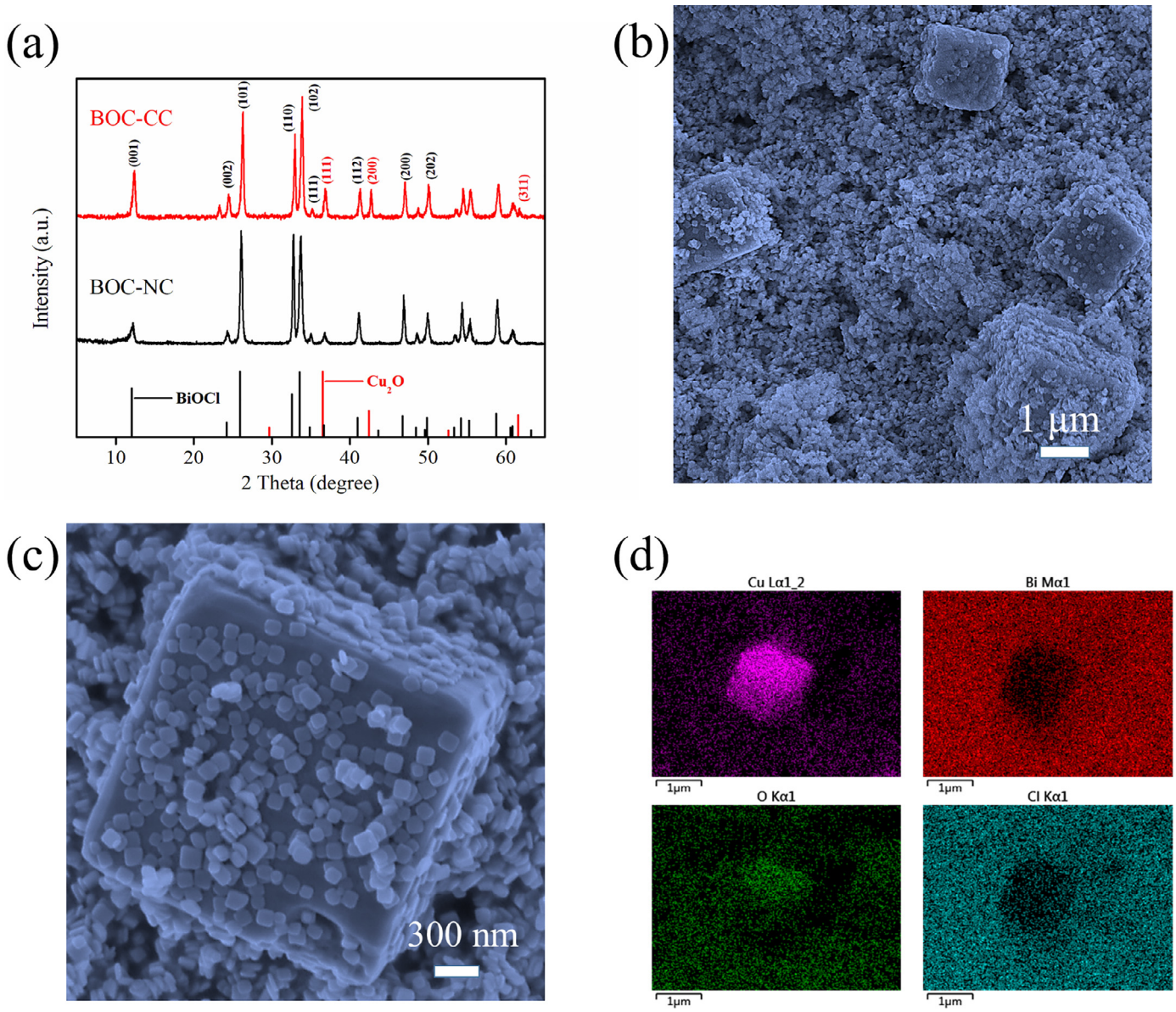

Fig. 1. (a) XRD patterns of BOC-CC and BOC-NC; (b) and (c) SEM images and (d) EDX mapping distribution of Cu, Bi, O and Cl elements of as-prepared BOC-CC.

2. Experimental

2.1. Synthesis procedures

All the reagents were of analytical-reagent grade and used without further purification. BiOCl was synthesized via a solvothermal method. In a typical procedure, 2.5 mmol $Bi(NO_3)_3{\cdot}5H_2O$ and 1 mmol $CuCl_2{\cdot}2H_2O$ were completely dissolved in 30 mL ethylene glycol (EG). Then, 5 mL NaOH (1 mol L^{-1}) aqueous solution was added by dropwise into the above solution. The mixture was stirred for 0.5 h at room temperature in air, then was transferred to a 50 mL Teflon-lined stainless steel autoclave, followed by heating and maintaining at 160 °C for 12 h, and then naturally cooled to ambient temperature. The as-prepared samples labeled as BOC-CC were washed with deionized water and ethanol thoroughly to remove residual ions and dried at 60 °C in air for 12 h for further characterization. The controlled experiment was carried out as same as the above-mentioned procedure besides replacing the addition of $CuCl_2{\cdot}2H_2O$ by NaCl as Cl source. The obtained product was labeled as BOC-NC.

2.2. Characterization

The composition and phase purity of the as-prepared samples were characterized by powder X-ray diffraction (XRD, D/max 2500, Cu Kα radiation). The XRD patterns were recorded within 2θ ranging from 5° to 65° at 0.02°/s. The morphologies and crystalline structures were determined using focused ion beam (Zeiss Auriga FIB/SEM) equipped with an energy-dispersive X-ray spectroscope (EDX) and transmission electron microscopy (TEM, Tecnai G2 F20).

3. Results and discussion

The crystalline structure and chemical composition of the as-prepared examples were obtained by powder X-ray diffraction (XRD), as shown in Fig. 1(a). The characteristic peaks of the BiOCl (JCPDS card no. 06-0249) could be easily observed, suggesting the formation of BiOCl of BOC-CC and BOC-NC. The narrow sharp peaks suggested that the products were highly crystalline. In addition, there were some other peaks marked by stars of XRD pattern of BOC-CC that corresponded to the JCPDS card (card no. 78-2076) of Cu_2O, implied that BOC-CC was a