Materials Science in Semiconductor Processing 41 (2016) 12–16

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Controllable hydrothermal synthesis of BiOCl nanoplates with high exposed {001} facets

Xiulan Hu [a,*,1], Yanqiu Xu [a,1], Haikui Zhu [a], Fengnan Hua [b], Shoufeng Zhu [a]

[a] College of Materials Science and Engineering, Nanjing Tech University, China
[b] Suzhou Tailida Technology Co., Ltd., Suzhou, China

ARTICLE INFO

Article history:
Received 22 March 2015
Received in revised form
4 August 2015
Accepted 6 August 2015

Keywords:
BiOCl
Microstructure
Sodium citrate

ABSTRACT

Square-like bismuth oxychloride (BiOCl) nanoplates with high exposed {001} facets were successfully synthesized through a facile hydrothermal process in the presence of sodium citrate. Citric anions reduce BiOCl nanoplate size and lead to high intensity ratio of (001)–(102) by selectively absorbing on the {001} facets of BiOCl nanoparticles or nanoplates. Size of BiOCl nanoplates decrease to about 200 nm when 1.5 mmol sodium citrate was added. Thickness of BiOCl nanoplates also decreases from 100 nm to about 45 nm with increasing sodium citrate amounts. Diffraction peak intensity ratio of (001)–(102) of BiOCl nanopaltes is up to 0.93 with the adding of 1.5 mmol sodium citrate. As-obtained BiOCl nanoplates show a higher photocatalytic activity for degrading methyl orange (MO) than that prepared without sodium citrate under simulated sunlight irradiation.

1. Introduction

Bismuth oxychloride (BiOCl) has drawn considerable attention for its potential applications as a novel photocatalyst under UV light illumination due to its wide optical bandgap (~3.5 eV) [1–3]. BiOCl exhibits higher activity for pollutant degradation than P25 under UV light and visible light illumination because of its unique layer structure and high chemical stability [4–6]. The tetragonal layered structure of BiOCl is consisted of [Cl–Bi–O–Bi–Cl] sheets stacked together by nonbonding interaction through Cl atoms along the *c*-axis [5], which results in a high thermodynamic stability and an efficient separation of photo-induced electron–hole pairs [7–9]. Recently, considerable attention has been paid to the facet-controlled fabrication of BiOCl because of its facet-dependent photocatalytic, photoelectric, and other surface-related properties [10–15]. Previous study clarified that nanosheets with exposed {001} facets exhibit higher activity for pollutant degradation under UV light irradiation due to their clear boundary of $[Bi_2O_2]^{2+}$ and halogen slabs. And {001} facets are considered to be the most favorable facets that influence photocatalytic reactivity due to their extremely high thermodynamic stability and low electron–hole recombination rate.

Thus, many researchers concentrated their attentions to study photocatalytic application of energetic {001} facets of BiOCl. Jiang et al. have selectively synthesized BiOCl nanosheets with exposed {001} and {010} facets by adjusting pH value via a facile hydrothermal route [14]. BiOCl nanosheets with tunable {001} facets percentages were successfully synthesized by hydrolyzing molecular precursors $Bi_n(Tu)_xCl_{3n}$. The {001} facets percentage can be controlled from 71% to 87% by adjusting the feed ratios of $BiCl_3$ [10].

However, to our knowledge, the effects of surfactants on controlling synthesis of BiOCl nanoplates with exposed {001} facets were not reported yet. In general, citrate is an important biological ligand for metal ions. It has been widely employed as a reluctant and capping agent in the synthesis of CuO, Ag and Ag–Au alloy nanoparticles [16–18], and also served as a shape controller and stabilizer in the synthesis of $Ni(OH)_2$, calcite, coated CdSe colloids, doughnut-shaped ZnO microparticles and CuI crystals [19–23]. In this study, sodium citrate was employed for the first time for controllable synthesis of BiOCl nanostructures with exposed {001} facets. Their photocatalytic activities for degrading methyl orange (MO) were investigated under simulated sunlight irradiation, too.

2. Materials and methods

2.1. Chemicals

Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) was purchased from Aladdin Reagent (China) Co., Ltd. Sodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) and potassium chloride (KCl) were purchased from Shanghai Lingfeng Chemical reagent Co., Ltd. Methyl orange

---

[*] Corresponding author. Fax: +86 25 8358 7260.
E-mail address: whoxiulan@163.com (X. Hu).
[1] Yanqiu Xu and Xiulan Hu are co-first authors.

http://dx.doi.org/10.1016/j.mssp.2015.08.016
1369-8001/

($C_{14}H_{14}N_3NaO_3S$) was purchased from Tianjin Chemical reagent Co., Ltd. All reagents were analytical grade. Distilled water was used as a solvent.

2.2. Synthesis

BiOCl nanoplates were synthesized through a facile hydrothermal method. In a typical procedure, $Bi(NO_3)_3 \cdot 5H_2O$ (5 mmol) and KCl (5 mmol) were dissolved in 80 mL distilled water at ambient temperature under magnetic stirring. To study the influence of sodium citrate, a predetermined amount of sodium citrate (0.25 mmol, 0.5 mmol, 0.75 mmol, 1.5 mmol, that is the molar ratio of SC/Bi^{3+} is 0.05, 0.1, 0.15, 0.3, respectively) were added into the above solutions. After stirring for 0.5 h, the well-dispersed mixture solution was transferred into 100 mL Teflon-lined stainless steel autoclaves to perform hydrothermal reaction at 160 °C for 12 h. After autoclave was cooled down to room temperature, the solid product was collected by centrifugation and washed with distilled water for several times, and then the wet products was dried at 60 °C for 12 h for characterization. Products obtained were denoted as BOC-1, BOC-2, BOC-3, BOC-4 and BOC-5, which corresponded to the amount of sodium citrate added was 0, 0.25 mmol, 0.5 mmol, 0.75 mmol, 1.5 mmol, respectively.

2.3. Characterization and photocatalytic activities

The composition of products was examined by X-ray powder diffraction (XRD) analysis which was carried out on a SmartLab diffractometer with high-intensity Cu-Kα (λ=1.54 Å). The morphologies and microstructures were observed by a field emission scanning electron microscope (FE-SEM, Hitachi, S-4800).

Photocatalytic activities of BiOCl were evaluated by photodegradation of methyl orange (MO) under simulated sunlight irradiation. As BiOCl could only be excited by ultraviolet light due to its wide optical bandgap (~3.5 eV) and that ultraviolet light only accounts for about 5% of sunlight, two kinds of 300 W Xe lamps (Beijing Perfectlight Technology Co., Ltd.) were used as light sources for comparison to study the influence of different intensity of ultraviolet light: PLS-SXE300UV (output powers of visible light and UV-light are 17.6 W and 6.6 W, respectively, named LS-1 in later), and PLS-SXE300BF (output powers of visible light and UV-light are 19.6 W and 2.6 W, respectively, named LS-2 in later). Experiments were carried out in a Pyrex photocatalytic reactor. The distance between the lamp and the liquid level of MO solution was 15 cm. In a typical photocatalytic experiment, 0.1 g BiOCl was well dispersed into 50 ml MO solution (10 mg L^{-1}) for LS-1 experiment. Based on the previous experimental results, 0.05 g BiOCl was well dispersed into 50 ml MO solution (10 mg L^{-1}) for LS-2 experiment due to their fast degradation rates in LS-1 experiment. Before irradiation, the suspension was stirred in the dark for 30 min to reach an adsorption–desorption equilibrium of MO on the catalyst surface. At a given time interval during irradiation, 3 ml clear liquor was taken out from suspension. The photocatalytic degradation of MO was monitored by measuring its absorbance in a wavelength range of 350–650 nm with a UV–vis spectrophotometer (UNIC, UV-4802S).

3. Results and discussions

3.1. Characterization

Fig. 1 shows XRD patterns of as-prepared BiOCl nanoplates with a different amount of sodium citrate. All diffraction peaks are readily indexed to tetragonal phase of BiOCl with lattice constants of $a=b=3.891$ Å, and $c=7.369$ Å (JCPDS Card no. 06-0249). No peaks of any other phases are detected, indicating that as-synthesized BiOCl products are pure. All strong diffraction peaks suggest that as-synthesized BiOCl are well-crystallized. BiOCl crystal has a layered structure characterized by $[Bi_2O_2]$ slabs which are interleaved by double slabs of Cl atoms, and the dominating facets of BiOCl crystal are (001) and (110) [10]. In the absence of sodium citrate, diffraction peak of (001) plane is weaker than those of other planes. When the amount of sodium citrate is more than 0.75 mmol, diffraction peak intensities of {001} facets family such as (001), (002) and (003) become stronger, indicating that BiOCl nanoplates should be favor to grow along the *c*-axis [001] orientations. The diffraction peak intensity ratios of (001)–(102) of BiOCl samples prepared with 0, 0.75 mmol and 1.5 mmol sodium citrate are 0.53, 0.78 and 0.93, respectively.

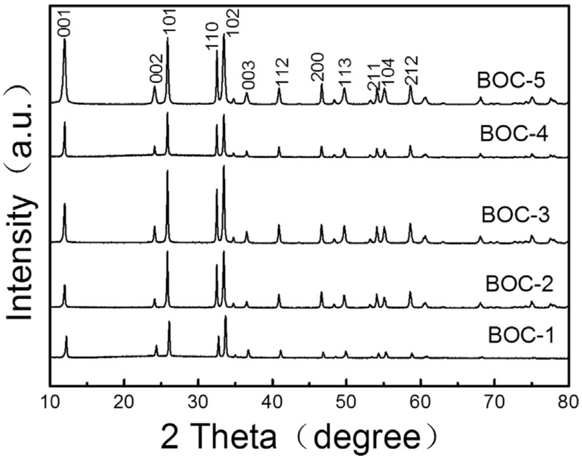

Fig. 1. XRD patterns of as-prepared BiOCl nanoplates with different amounts of sodium citrate. BOC-1, BOC-2, BOC-3, BOC-4 and BOC-5 are corresponded to the amount of sodium citrate added is 0, 0.25 mmol, 0.5 mmol, 0.75 mmol, 1.5 mmol, respectively.

Fig. 2 shows SEM images of BiOCl synthesized at 160 °C for 12 h with various amounts of sodium citrate. As shown in Fig. 2a, BiOCl obtained without sodium citrate consists of numerous irregular nanoplates with a diameter of about 0.3–2 μm and an average thickness of about 100 nm. Whereas BiOCl nanoplates obtained in the presence of sodium citrate have a square-like morphology as shown in Fig. 2b–d. What's more, the particle size and thickness of BiOCl decrease with increasing amount of sodium citrate. When sodium citrate is up to 1.5 mmol, the average size of BiOCl nanoplates is only about 200 nm, and the thickness of BiOCl nanoplates decreases to 45 nm (Fig. 2d).

All of above results clarified that sodium citrate has a significant effect on morphology and microstructure of BiOCl nanoplates. The possible formation mechanism of smaller BiOCl nanoplates with high exposure of {001} facets could be understood with the following reactions:

$$2Bi^{3+} + 2H_2O \leftrightarrow [Bi_2O_2]^{2+} + 4H^{+} \quad (1)$$

$$[Bi_2O_2]^{2+} + 2Cl^{-} \leftrightarrow 2BiOCl \quad (2)$$

First, Bi^{3+} was produced after $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in distilled water, Bi^{3+} cations are inclined to react with H_2O to yield $[Bi_2O_2]^{2+}$ and H^{+} cations at the beginning (Eq. (1)). Then negative Cl^{-} anions will combine with positive $[Bi_2O_2]^{2+}$ cations to form numerous small crystalline nuclei of Cl–Bi–O–Bi–Cl due to the coulomb coupling force, within which the interactions of Bi and O involve covalent bonds (Eq. (2)). When sodium citrate was added, citrate ions may bond to $[Bi_2O_2]^{2+}$ of {001} surfaces through the –COO– and –OH functions. In this way, citric anions could absorb on