Synthesis and Characterizations of BiOCl Sheets

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BiOCl sheets with tetragonal structure have been successfully synthesized via a hydrothermal route using BiCl₃ as the starting materials. The samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and photoluminescence (PL) spectrum. The diameter and thickness of the BiOCl sheets can be adjusted by controlling the hydrothermal temperature and growth time. And BiOCl nanosheets can be obtained. PL spectrum of the BiOCl sheets shows blue light and green light emission, indicating potential application in optical devices. [DOI: 10.1380/ejssnt.2012.161]

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I. INTRODUCTION

Bismuth and its compounds have attracted great research interest owing to their unique qualities [1, 2]. Among them, bismuth oxyhalide semiconductors, such as BiOCl, Bi₂O₂Cl₂, Bi₂O₃Cl₁₀, Bi₅O₄Cl and Bi₁₂O₁₇Cl₂ have demonstrated excellent photocatalytic activities and optical properties offering a new family of promising photocatalysts [3–5]. BiOCl is a wide bandgap semiconductor (Eg = 3.46 eV) with a tetragonal PbFCl-type structure. BiOCl crystallizes into unique layered structures consisting of [Cl–Bi–O–Bi–Cl] sheets stacked together by the nonbonding interaction through the Cl atoms along the c-axis. BiOCl has good electrical, optical and mechanical properties due to the strong intralayer bonding and weak interlayer van der Waals interaction resulting in the promising application potential in cosmetics, pharmaceuticals, battery cathodes, photocatalysis and photoelectrochemical devices [6]. Because of the unique layered structure and high photocorrosion stabilities in the presence of redox pairs, BiOCl has recently been shown as a novel material for photocatalysis and photoelectrochemical cells [7]. In addition, BiOCl exhibits catalytic properties for the oxidative cracking of n-butane to lower alkenes [8].

In present, most of the reported synthesis methods for the BiOCl structure are wet chemical methods [9–11]. BiOCl lamellae has also been synthesized via a sonochemical method in a surfactant/ligand-free solution [12]. A sovothermal method was used previously for synthesizing BiOCl nanostructures [13]. BiOCl nanostructures have also been synthesized by a low temperature chemical vapor transport of a AuCl₃/Bi mixture on different substrates [6]. However, these methods have not received much commercial importance because of the use of expensive raw materials and many processing steps. Therefore, it is great significance for synthesizing BiOCl sheets by a simple and facile method at low cost.

In the paper, a simple, efficient, low-cost hydrothermal method has been used to synthesize BiOCl sheet-shaped structures using BiCl₃ as Bi source material. The roles of the growth conditions on the formation of the BiOCl sheets have been investigated in detail. The photoluminescence of the BiOCl sheets shows strong emission peaks suggesting good optical properties.

II. EXPERIMENTAL

High pure BiCl₃ powder (AR grade, purity: ≥99.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd. of China. The starting material BiCl₃ was used without further purification. In a typical procedure, 0.6 g BiCl₃ was dissolved in 60 mL deionized water. The BiCl₃ solution was placed in a 100 mL autoclave with a Teflon liner. The autoclave was maintained at room temperature-180°C for 0.5-24 h. Subsequently the autoclave was cooled naturally in air. The resulting white precipitates were filtered, washed with deionized water for several times and dried at 60°C in air. Finally, the white BiOCl powders were obtained.

The obtained products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and photoluminescence (PL) spectrum. XRD pattern was carried out on a Bruker AXS D8 X-ray diffractometer equipped with a graphite monochromatized Cu-Kα radiation (λ = 1.5406 Å). The samples were scanned at a scanning rate of 0.05°/s in the 20 range of 20-80°. SEM observation was performed using JEOJ EM-640LV SEM with a 15-KV accelerating voltage. FTIR spectroscopy (Perkin Elmer PE, WQF-410 spectrometer) was used at room temperature in the range of 450-4000 cm⁻¹ with a resolution of 4 cm⁻¹. PL measurement was carried out at room temperature using 235 nm as the excitation wavelength with a luminescence spectrometer (Cary Eclipse) in the range of 350-600 nm.

III. RESULTS AND DISCUSSIONS

The XRD pattern of the product is shown in Fig. 1. The experimental XRD profile taken from the BiOCl sample shows that all of the diffraction peaks can be indexed as the tetragonal BiOCl phase (JCPDS card, No. 06-0249). No peaks of any other phases are observed indicating that the BiOCl products are highly pure single phase structure. In addition, the intense and sharp diffraction peaks sug-
FIG. 1: X-ray diffraction pattern of the BiOCl sheets synthesized from 180°C for 24 h.

Figure 2 shows the morphology and size of the BiOCl product. The product exhibits circular sheet-shaped structure with the diameter in the range of 1-10 μm (Fig. 2(a)). The morphology of the BiOCl sheets is similar to that of the BiOCl nanostructures synthesized by vapor transport method [7]. The diameter of most of the BiOCl sheets is about 3 μm. And a small amount of BiOCl sheets have the diameter of about 10 μm. The thickness of sheets of the BiOCl sheets is about 500 nm (Fig. 2(b)).

Figure 3 shows the FTIR spectrum of the BiOCl sheets in the 450-4000 cm⁻¹ region. The weak bands appearing in the range of 3200-3800 cm⁻¹ with the absorption peak at 3733.51 cm⁻¹ are assigned to the H–O–H stretching from water. The weak bands at 1627.23 cm⁻¹ and 1398.14 cm⁻¹ are due to adsorbed atmospheric CO₂, which results from the preparation and processing of FTIR sample in the ambient atmosphere [14]. The band at 524.54 cm⁻¹ is assigned to Bi–O bands [4].

The formation of the sheet-shaped structure is generally considered to be a self-assemble process. Suitable templates, such as hard and soft templates are also commonly used [15, 16] for the synthesis of BiOCl sheet-shaped structure. BiOCl sheet-shaped microspheres have been synthesized using ethylene glycol as the solvent and a soft template by the hydrothermal method [7]. BiOCl micro/nanostructures can also be obtained by the hydrothermal method with poly(vinylpyrrolidone) (PVP) as the surfactant [17]. In order to analyze the formation process of the BiOCl sheets, the growth condition (temperature, time and compactness) dependences on the formation of the BiOCl sheets are researched.

The temperature dependence results on the formation of the BiOCl sheets at different hydrothermal temperature for 24 h are shown in Fig. 4. The circular sheet-shaped morphology of the BiOCl sheets (Figs. 4(a) and 4(b)) is same when the hydrothermal temperature decreases to 120°C. However, the diameter and thickness of the BiOCl sheets decrease to less than 1 μm and about 50 nm, respectively. The result shows that the BiOCl product is composed of nanosheet-shaped structure. With the hydrothermal temperature further decreases to 80°C and room temperature, the amount of the BiOCl sheets decreases obviously and the BiOCl product is composed of mainly irregular particles (Figs. 4(c) and 4(d)). The temperature dependence results show that the temperature plays an essential role on the formation and growth of the BiOCl sheets. A small amount of BiOCl sheets still exist in the product when the experiment was conducted.
FIG. 4: Temperature dependence on the formation of the BiOCl sheets at different hydrothermal temperature for 24 h. (a) and (b) 120°C, (c) 80°C, and (d) room temperature.

FIG. 5: Time dependence on the formation of the BiOCl sheets at 180°C for different time. (a) and (b) 12 h, (c) 6 h, and (d) 0.5 h.

FIG. 6: Compactness dependence on the formation of the BiOCl sheets under the hydrothermal conditions of 180°C for 24 h. (a) and (b) 20 vol% compactness, (c) and (d) 80 vol% compactness.

determined by the volume ratio of water in the autoclave which is called compactness. Therefore, the compactness dependence on the formation of the BiOCl sheets is analyzed. The corresponding results are shown in Fig. 6. The BiOCl sheets with similar morphology and size are obtained when adjusting the compactness to be 20 vol% (Figs. 6(a) and 6(b)) and 80 vol% (Figs. 6(c) and 6(d)). The result shows that the compactness in the autoclave has no obvious effect on the formation of the BiOCl sheets.

The growth condition dependence results further show that the size of the BiOCl sheets can be adjusted by controlling the hydrothermal temperature and growth time. The BiOCl sheets with nanoscale structures can also obtained. In addition, no templates including hard and soft templates were used in the work. The formation and growth of the BiOCl sheets are considered preferred to be a nucleation and crystallization process rather than a simple self-assembled growth process which is similar to the flower-shaped BiOCl film and BiOCl nanoplates [18, 19]. At the initial formation stage of the BiOCl sheets, BiCl₃ and H₂O react to form BiOCl and HCl under the hydrothermal conditions. BiOCl crystallizes into unique layered structures consisting of [Cl–Bi–O–Bi–Cl] sheets stacked together by the nonbonding interaction through the Cl atoms along the c-axis. Therefore, the BiOCl nanoparticles spontaneously appear in the supersaturated solution which serve as the nuclei for the formation of the BiOCl nanosheets. The BiOCl nanosheets grow continuously with the increase of the hydrothermal temperature and time resulting in the final formation of the BiOCl sheets with different size.

Figure 7 shows the room temperature PL spectrum of the BiOCl sheets synthesized from 180°C for 24 h. The PL spectrum exhibits strong blue light emission centered at 422 nm, 472 nm, and 488 nm, and a poor green light emission centered at 530 nm. The similar PL emission bands are also observed from the Bi₂O₃ and BiOCl film which exhibits strong PL emission peaks centered at 438 nm, 460 nm, 484 nm, and 536 nm [18, 20]. Therefore,
it is considered that the PL emission of the BiOCl sheets is closely relative to the Bi–O.

IV. CONCLUSIONS

In summary, a simple and facile hydrothermal route has been used to synthesize BiOCl sheets with tetragonal structure using BiCl$_3$ as the Bi source material. BiOCl sheets with different diameter and thickness can be obtained by controlling the hydrothermal conditions. The diameter and thickness of the BiOCl sheets are 150 nm–10 μm and 50–500 nm, respectively. The blue light and green light emission in the PL spectrum exhibits potential application in optical devices. The hydrothermal method has the advantages of simple process, low cost and easily controllable mass production.

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