## DOI: 10.1021/cg900940s

# Ionothermal Synthesis of BiOCl Nanostructures via a Long-Chain Ionic Liquid Precursor Route

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Received August 9, 2009; Revised Manuscript Received April 28, 2010

**ABSTRACT:** Ultrathin BiOCl nanoflakes, nanoplate arrays, and curved nanoplates have been successfully synthesized via an ionothermal synthetic route by using an ionic liquid 1-hexadecyl-3-methylimidazolium chloride ( $[C_{16}Mim]Cl$ ) as "all-in-one" solvent, simply adjusting reaction temperature. The samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM) and Fourier transform infrared spectroscopy (FT-IR), separately. Possible formation mechanisms of various nanostructures were proposed in terms of crystal growth habit and dynamics. In addition, the excellent adsorption performance of the asprepared BiOCl nanoplates makes them useful with potential applications in the aspect of wastewater treatment.

#### 1. Introduction

Ionic liquids (ILs) have been widely used in various fields not only due to their unique properties such as negligible vapor pressure and thermal stability but also because of their tunable properties and designable structures.<sup>1</sup> The designable feature of ILs is very suitable to the synthesis of inorganic nanomaterials, for inorganic chemical processes are extremely diverse. In recent years, many IL-involved processes, including electrodeposition,<sup>2</sup> photochemical reduction,<sup>3</sup> electron beam irradiation,<sup>4</sup> sol-gel,<sup>5</sup> solvothermal,<sup>6</sup> and ionothermal route,<sup>7</sup> have been developed to synthesize inorganic nanostructures. Among them, ionothermal synthesis is one of the most promising methods. Ionothermal synthesis has been developed into a versatile and advantageous synthesis technique.<sup>7</sup> Compared to traditional hydro/solvothermal synthesis, ionothermal synthesis has two advantageous features: the ionic reaction medium can uniquely influence the course of chemical reactions; ionic liquids can act as "all-inone" solvent/template for the synthesis of inorganic materials, which enables the synthesis of inorganic materials with novel and improved properties.8

ILs derived from 1-alkyl-3-methylimidazolium are of particular interest because, by changing the alkyl chain length or the anion, a wide variation of properties such as hydrophobicity, viscosity, density and salvation strength can be obtained.<sup>9</sup> The long-chain ILs display the behavior of both lyotropic and thermotropic liquid crystalline,10 and the amphiphlic ILs' derivatives could bring out ordered self-organized structures.<sup>10a,11</sup> For example, Zhou et al. demonstrated that the long-chain 1-hexadecyl-3-methylimidazolium chloride ([C<sub>16</sub>Mim]Cl) displayed significantly stronger tendency toward self-aggregation and supramolecular templating in the preparation of supermicroporous lamellar silica by nanocasting, owing to the distinct polarizability of the head groups and the special high-concentration phases of those ILs.<sup>12</sup> Wang et al. and Adams et al. found that long-chain ILs could be used to generate mesoporous silica with a 2D hexagonal structure



of cylindrical mesopores using hydrothermal synthesis approuach, respectively.<sup>13</sup> To the best of our knowledge, however, there is no report on long-chain ILs employed in ionothermal synthesis as solvent and precursor.

BiOCl has drawn considerable attention because of its optical properties and promising inductrustrial applications, such as catalysts and photocatalysts,<sup>14</sup> ferroelectreic materials,<sup>15</sup> pigments,<sup>16</sup> photoluminescence,<sup>17</sup> and so on. Inspired by their excellent properties, there is thus considerable interest in improved BiOCl systems. Various nanostructures including: nanoplatelet, nanobelts, nanowires, and nanoflowers, have been fabricated via various synthetic routes, such as hydro/solvothermal method,<sup>18</sup> low-temperature vapor-phase synthesis,<sup>19</sup> electrospinning,<sup>14e</sup> and reverse micromulsions,<sup>20</sup> sonochemical synthesis.<sup>21</sup> Although well-defined nanostructures of BiOCl have been fabricated, it is still a big challenge to develop an alternative route to fabricate BiOCl nanostructures with novel morphologies and improved properties.

Herein, we have reported the ionothermal synthesis of the ultrathin BiOCl nanoplatelets, nanoplate arrayes and curving nanoplates at different reaction temperatures. Furthermore, the formation mechanism of BiOCl nanostructures have been rationally explained in terms of crystal growth habit and dynamics. It is expected that this ionothermal synthesis using long-chain ionic liquid could be used to fabricate other polar nanomaterials with novel morphologies and improved properties in the fields of optics, electrochemistry, and catalysis. Moreover, experimental results demonstrated that the assynthesized BiOCl nanoplates had a high adsorption capacity and high adsorption efficence, compared with some other nanomaterials in the neutral media. We expect that the assynthesized BiOCl nanoplates would be promisingly applied to adsorp heavy metal ions in the field of wastewater treatment.

#### 2. Experimental Section

**2.1.** Synthesis of Ionic Liquid 1-Hexadecyl-3-methylimidazolium Chloride ( $[C_{16}Mim]Cl$ ).  $[C_{16}Mim]Cl$  was synthesized according to reported procedures,<sup>22</sup> 0.25 mol of 1-hexadecyl chloride and 0.25 mol of 1-methylimidazole were mixed and refluxed at 363 K for 24 h,

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then cooled to room temperature to obtain a waxy white solid, which was dispersed in THF to recrystallize, and then washed with THF three times. A white powder product was collected and dried under a vacuum at room temperature.

**2.2.** Synthesis of BiOCl Nanostructures. In a typical synthesis, 1.0 mmol of  $Bi(NO_3)_3 \cdot 5H_2O$  and 10 mmol of  $[C_{16}Mim]Cl$  were mixed together, then transferred into a 20 mL Teflon-lined stainless autoclave. The autoclave was heated at 180 °C for 12 h, and then naturally cooled to room temperature. The resulting precipitates were collected and washed with ethanol and deionized water thoroughly and dried at 50 °C in air. To investigate the effect of reaction temperature, we also conducted ionothermal reactions at 120 and 200 °C.

**2.3. Characterization.** The X-ray diffraction (XRD) patterns of the products were recorded with Rigaku D/max Diffraction System using a Cu K $\alpha$  source ( $\lambda = 0.15406$  nm). The scanning electron microscopy (SEM) images were taken with a JEOLJSM-6700F field-emission scanning electron microscope (15 kV). The high-resolution transmission electron microscopy (HR-TEM) images were taken on a JEOL 2010 high-resolution transmission electron microscope performed at 200 kV. The specimen of HR-TEM measurement was prepared via spreading a droplet of ethanol suspension onto a copper grid, coated with a thin layer of amorphous carbon film, and allowed to dry in air.

**2.4. Water Treatment Experiments.** The adsorption studies were performed by mixing 0.1 g BiOCl nanoplates with 50 mL of  $K_2Cr_2O_7$  solution in a 100 mL stopper conical flask. Standard acid of 0.1 M HNO<sub>3</sub> solution was used for pH adjustment. All the adsorption experiments were carried out at room temperature and



Figure 1. XRD pattern of BiOCl nanoplates obtained at 180 °C for 24 h.

pH of 2.5. UV-vis adsorption spectra (Shimadzu UV-1601PC) were recorded at different intervals to monitor the process.

### 3. Results and Discussion

**3.1. Characterization of Structure and Morphology.** Figure 1 shows the typical XRD pattern of the as-synthesized 2D BiOCl nanoplatelets. The experimental XRD profile taken from the assynthesized BiOCl samples shows that all of the peaks may be indexed as the tetragonal phase BiOCl (cell constants a = 3.89 Å, c = 7.37 Å; JCPDS File No. 06–0249). No peaks of any other phases were detected, indicating that the products are very high-purity, single-phase samples. In addition, the intense and sharp diffraction peaks suggest that the as-synthesized products are well-crystallized. The corresponding energy-dispersive X-ray spectrum (EDS) (see Figure S1 in the Supporting Information) further indicates that the products consist of Bi, O and Cl with a ratio of about 1:1:1, which is consistent with the stoichiometric BiOCl.

The morphology of as-prepared BiOCl nanoflakes were characterized by SEM and TEM technique. Images a and b in Figure 2show the morphology of as-prepared BiOCl nanoflakes. As shown in Figure 2a, the sample is composed of almost uniform nanoplates. Further investigation found that the average thickness of BiOCl nanoflakes was about 18 nm and the edge is not very smooth, as shown in Figure 2b. The delicate structure of BiOCl nanoflakes was further characterized by TEM. Figure 2c shows the ultrathin BiOCl nanoflakes. The corresponding fast Fourier transformation (FFT) image of BiOCl (inset of Figure 3d) indicates that the layered structure is perpendicular to the c axis. The HRTEM image of a single BiOCl nanoflake (Figure 3d) exhibits good crystalline and clear lattice fringes. The interplanar spacing is 0.275 nm corresponding to the  $\{110\}$  planes of the tetragonal system of BiOCl. The HRTEM observation confirms that these BiOCl lamellae are perpendicular to the c axis, which is well according to the XRD result.

**3.2. Formation Mechanism of BiOCl nanoplates.** Although plates are typically observed for BiOCl, the ultrathin nanoplate



Figure 2. (a, b) SEM images; (c) TEM image and (d) HR-TEM image of BiOCl nanoplates obtained at 180 °C for 24 h. Inset: its corresponding fast Fourier transform (FFT) image.



Figure 3. (a) Clinographic projection of the unit cell of BiOCl; (b) clinographic projection of the coordination polyhedron around Bi.

is not easily obtained. Therefore, template effect of [C<sub>16</sub>Mim]Cl should be taken into account. Under this synthetic condition, [C<sub>16</sub>Mim]Cl not only acts as reactant and solvent, but may also play a crucial role on the shape of the BiOCl as a soft template and a capping agent. In recent years, based on the special molecular structure and properties of the longchain ILs, some IL-crystal precursors containing organic matrix have been used as templates in the synthesis system.<sup>23</sup> In the present case, the formation of the ultrathin flakelike BiOCl can be possibly explained from the view of crystal growth habit and dynamics. The BiOCl has a tetrahedron structure (the unit cell of BiOCl shown in Figure 3a), which can derive from the fluorite (CaF<sub>2</sub>) structure.<sup>24</sup> Figure 3b shows the clinographic projection of the coordination polyhedron around Bi. In Figure 3b, each Bi atom is eightcoordinated by four O atoms and four Cl atoms in the form of an asymmetric decahedron. The decahedra are linked to each other by a common O- Cl edge along the a and b axes forming infinite layers. Figure 3b also shows the coordination of O and Cl. Each O atom is linked to four Bi atoms, forming a tetragonal pyramid with the O atom at its apex. Also each Cl atoms forms with the neighboring Bi atoms. A tetragonal pyramid with the Cl atom at its apex. Neighboring decahedra form layers along (001), which are connected by common O-Cl edges. Neighboring layers of decahedra are connected by common O-O or Cl-Cl edges. The [BiOCl] layers are stacked together by the van der Waals forces through the Cl atoms along the c-axis.14f Therefore, the structure is not closely packed in this direction, and the *ab* plane of BiOCl is favorable by the preferred adsorption of  $[C_{16}Mim]^+$  cations. The alkyl imidazolium ion is part of the solvent and a structure-directing agent for the crystallization. Along with the  $Cl^-$ ,  $[C_{16}Mim]^+$  will be also aligned and arrayed along the BiOCl layer, driven by the coulomb coupling force with the Cl. It is reasonable to deduce that the [C<sub>16</sub>Mim]Cl, which is therefore a supramolecular solvent that has ordered structures similar to those in literatures, <sup>23a,25</sup> is selectively adsorbed on the (001) plane of BiOCl to effectively inhibit crystalline growth in the [001] direction. Therefore, the growth of BiOCl crystals are inhibited along the *c*-axis to form thin BiOCl nanoflakes. The interaction between BiOCl crystal planes and the heads of  $[C_{16}Mim]Cl$  can be schematically illustrated in Scheme 1. To investigate the role of ionothermal parameters, controlled experiment was conducted under hydrothermal condition. BiOCl nanoplates with a thickness of about 50 nm (see Figure S2 in the Supporting Information) can be obtained when reaction other parameters kept the same except the solvent and

Scheme 1. Schematic Illustration of the Interaction of Biocl Crystal Planes and the Head Parts of [C<sub>16</sub>Mim]Cl



chlorine source being replaced by distilled water and 1 mmol of  $[C_{16}Mim]Cl$ . The experimental results indicate that ionothermal process is vital to obtain ultrathin BiOCl nanoplates.

3.3. Influence of Reaction Temperature. Reaction temperature played a crucial role in determining the morphologies of BiOCl nanostructures. Curved nanoplates (Figure 4a,b) could be obtained when the reaction was performed at 200 °C while other condition kept constant. In images a and b in Figure 4, the average thickness of curved nanoplates is about 14 nm, which is thinner than that of nanoplates synthesized at 180 °C. The curving of BiOCl nanoplates could be well-explained as follows: as we know, the lamellar BiOCl possessed twodimensional layered structures. The edges of the lamellar products might have many atoms with dangling bonds, and they should possess enough energy to destabilize the twodimensional structures. To minimize the total surface energy, the lamellar BiOCl tends to bend to form curved nanoplates by saturating these dangling bonds, which is similar to the reported literature.26

One the other hand, nanoplate arrays (Figure 5a, b) could be obtained when reaction was conducted at low temperature (120 °C). In Figure 5b, the thickness of nanoplates of nanoplate arrays is about 32 nm. The formation of nanoplate arrays might be attributed to the state of ionic liquid  $[C_{16}Mim]Cl$  at lower temperature. It is well accepted that  $[C_{16}Mim]Cl$  is one of special liquid crystals. The liquid crystal phase has properties and characteristics of the solid state and of the liquid state. In a liquid crystal, the molecules are oriented around a preferred direction. When reaction temperature was carried out at low temperature (120 °C), the



Figure 4. (a, b) SEM images, and (c) XRD pattern of as-synthesized BiOCl curved nanoplates.



Figure 5. (a, b) SEM images, and (c) XRD pattern of samples synthesized at 120 °C.

reaction solvent temperature [C<sub>16</sub>Mim]Cl is more preferred to keep characteristics of its solid state, in which the ionic liquid is relative fixed and can not freely move. Therefore, when reactants and product such as Cl<sup>-</sup>, Bi<sup>3+</sup>, H<sub>2</sub>O, and final products are transferred more slower, the aggregated phenomenon would appear, and thus nanoplate arrays would be produced. Furthermore, the XRD data (Figure 5c) shows that the assynthesized samples are composed of a series of bismuth oxide chlorides including: Bi<sub>4</sub>O<sub>5</sub>Cl<sub>2</sub> (PDF: 41–0658), Bi<sub>3</sub>O<sub>4</sub>Cl (36–0760), and BiOCl (PDF: 06–0249). In summary, influence of the reaction temperature on the morphology and compositions of BiOCl is closely related to the state of ionic liquid [C<sub>16</sub>Mim]Cl.

**3.4.** Application in Water Treatment. In recent years, considerable attention has been paid to the environmental problems involving water treatment. Compared with the traditional methods, the development of nanoscience and nanotechnology offers an alternative by using nanosorbents, nanocatalysts, bioactive nanoparticles, catalytic membranes with nanostructures, and so on for the resolution or amelioration of current water-treatment problems. Because of the good chemical stability, low cost, and large surface area of the as-synthesized BiOCl product, we expect it to be useful in the water treatments. Moreover, because the size of the BiOCl nanoplates was not too small, the solid/liquid separation would be easily realized by a facile method such as centrifugation.

Herein, we used the as-obtained BiOCl nanoplates to investigate their applications in water treatments. Potassium dichromate ( $K_2Cr_2O_7$ ) is considered highly toxic pollutants in water resources,<sup>27</sup> and their efficient removal from water is of great importance. In our experiments, 0.1 g of the as-obtained BiOCl nanoplates was added into 50 mL solutions with the initial concentrations of Cr(VI) being set at 40 mg/L and adjusted to pH 2.5 at room temperature (25 °C). Figure 6 shows the changes of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> concentration versus time. It



**Figure 6.** UV-vis absorption spectra of  $K_2Cr_2O_7$  solutions after treated with BiOCl nanoplates at different time intervals.

can be seen from the curve that the adsorption is rapid initially, and nearly 40% of the  $Cr_2O_7^{2-}$  can be absorbed in a short time. Calculated from the patterns, the removal capacities of Cr(VI) are 32 mg/g for the BiOCl nanoplates. The experimental results demonstrate that the adsorption performance of BiOCl nanoplates for  $Cr_2O_7^{2-}$  is better than that of mesoporous flowerlike NiO.<sup>28</sup> The difference is attributed to the different pH, for lower pH was favored by the adsorption. The mechanism for the removal of the  $\operatorname{Cr}_2 \operatorname{O}_7^{2-}$  contaminant can be explained from the perspective of surface chemistry in aqueous phase. The surfaces of metal oxides are generally covered with hydroxyl groups that vary in forms at different pH. The surface charge is neutral at pHzpc. Belowthe pHzpc, the adsorbent surface is positively charged, anion adsorption occurs.<sup>29</sup> These phenomena further proved that the adsorption of the metal ions may be a surface absorption process.

#### 4. Conclusion

In conclusion, this paper present a novel procedure for the synthetic BiOCl with different nanostructures, such as ultrathin

nanoplates, curved nanoplates and nanoplate arrays. Reaction temperature was found to play a crucial role in determining the morphologies of BiOCl nanostructures. This ionothermal synthetic route using long-chain ionic liquid has potential application in fabricating other polar nanomaterials with novel morphologies and improved properties in aspects of optics, electrochemistry, and catalysis. Moreover, the assynthesized BiOCl nanoplates would be promisingly applied to adsorp heavy metal ions in the field of wastewater treatment.

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China (20571044 and 20971070).

**Supporting Information Available:** Additional figures (PDF). This material is available free of charge via the Internet at http:// pubs.acs.org.

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