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Ionic-liquid assisted ultrasonic synthesis of BiOCl with controllable morphology and enhanced visible light and sunlight photocatalytic activity

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ABSTRACT

Ionic liquid assisted ultrasonic method was developed to prepare BiOCl at room temperature in a short time. Through this method, BiOCl with different controllable morphologies can be easily obtained via the simple change of the reaction solvents. The flowerlike microspheres, sheet and plate morphologies have been prepared in DMF, ethanol and water, respectively. And the as-prepared BiOCl samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), N_2 absorption-desorption isotherms and UV–vis diffuse reflectance spectroscopy. The photocatalytic activity of the as-prepared samples was evaluated towards degradation of Rhodomine B (RhB), Quinoline blue (QB) and methyl orange (MO). The results indicate that the as-prepared BiOCl samples have high photoactivities for the degradation of dyes both under the visible light irradiation and sunlight irradiation.

1. Introduction

Bismuth oxychloride (BiOCl), a ternary semiconductor with a wide band gap of 3.5 eV, has been found to be a promising material for organic matter degradation due to the unique and excellent electrical, magnetic, optical, luminescent and catalytic properties [1]. Its properties highly depend on the morphology [2]. Therefore, the development of morphological multiplicity is crucial for the photocatalytic applications, and the synthetic method is also required to be expanded. Recently, considerable attention has been paid to prepare BiOCl nanowires [3], nanosheets [4], nanoparticles [5], nanoplates [6], and nanoflowers [7]. And the synthetic methods used were always solvothermal method [5a,8], templates assisted method [3a,3b], hydrolytic method [7a,9], electrochemical method [10], sonochemistry [11], ionothermal synthesis [12], microwave-assisted method [13] and so on. However, the methods mentioned above are often conducted under annoying conditions, such as high reaction temperature, high pressure, long reaction time, and high degree of acidity or alkalinity. Therefore, developing a novel simple method to prepare BiOCl with different morphologies under mild conditions is much desired.

Herein, we have developed a novel and simple method namely ionic liquid assisted ultrasonic method to prepare BiOCl with different controllable morphologies at room temperature in a short time. Through this novel method, different morphologies, such as flowerlike microspheres, sheet and plate, can be easily obtained just by the simple change of reaction solvents under ultrasonic conditions. And the obtained BiOCl samples have high photocatalytic activities for the degradation of dyes both under visible light irradiation and sunlight irradiation.

2. Experimental

2.1. Materials

All the reagents in the present work were analytical grade and used without further purification.

2.2. Preparation

$Bi(NO_3)_3{\cdot}5H_2O$ (4.851 g, 10 mmol) and the ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) (2.0 g, 11.5 mmol) were first dispersed in solvents (30 mL), then the mixture was kept stirring for 20 min at room temperature and followed by ultrasonic irradiation for 10 min, and the precipitate was obtained by filtered and washed with water and ethanol several times. Finally, the prod-

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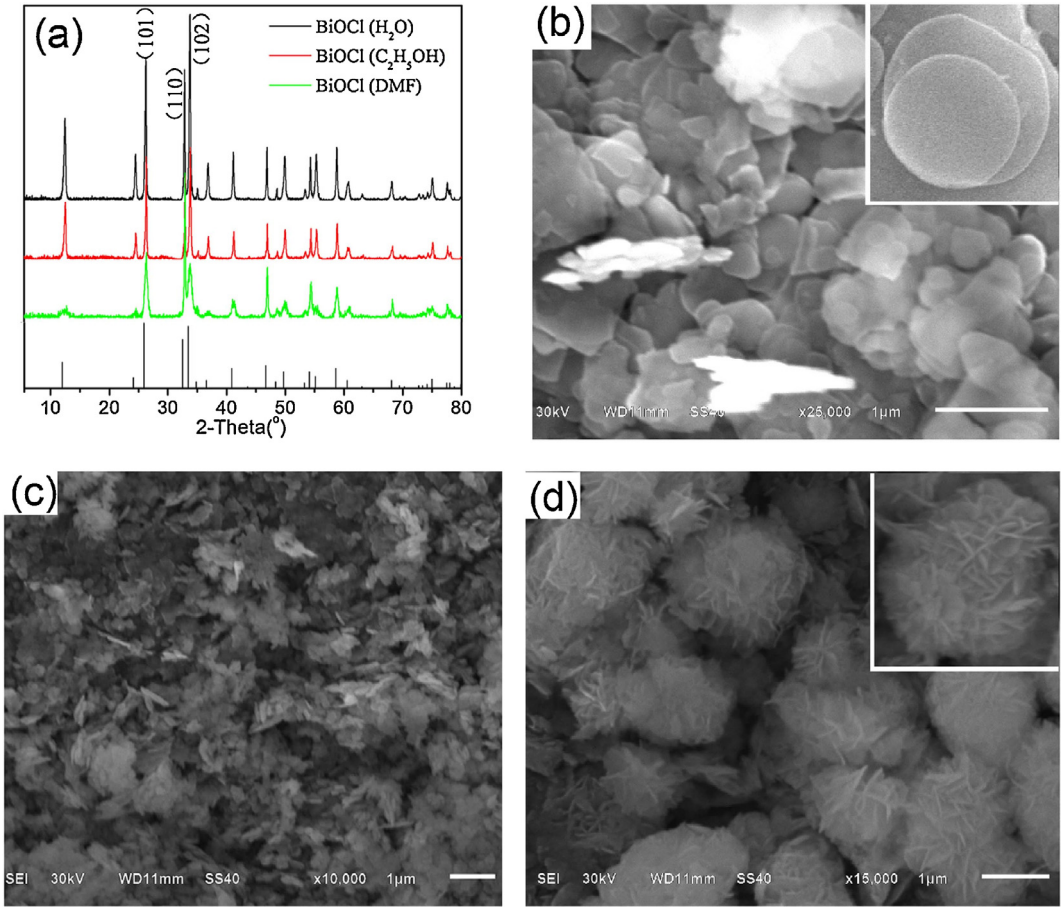

Fig. 1. (a) XRD pattern of the as-prepared BiOCl in different solvents via ionic liquid assisted ultrasonic method, SEM images of as-prepared BiOCl synthesized in (b) water, (c) ethanol, and (d) DMF.

uct BiOCl as a white powder was dried in a vacuum oven at 70 °C for 12 h.

2.3. Characterization

The X-ray diffraction (XRD) of BiOCl products was obtained on a D8 ADVANCE apparatus diffractometer using Cu Kα radiation, operated at 40 kV and 40 mA. Scanning electron microscope (SEM) (a JEOL JSM-6700F) was used to observe the morphology of the BiOCl products. The Brunauer–Emmett–Teller (BET) surface area was obtained on a TRISTAR II3020 nitrogen adsorption apparatus. UV–vis diffuse reflectance spectra was measured by a Shimadzu UV 2550 spectrophotometer, using $BaSO_4$ as a reference, which were recorded in the range of 200–800 nm.

2.4. Photocatalytic activity measurement

Rhodamine B (RhB), Quinoline blue (QB) and methyl orange (MO) solution (10 mg/L, 50 mL) were selected as model chemicals to evaluate the photocatalytic activity of the samples (50 mg) both under the visible lights irradiation (Xe-lamp, 300 W) with the 400 nm cutoff filter and sunlight (Xiangtan, China, 2014/09/21, 14:00–15:00) irradiation for a period time. All of the suspensions were magnetically stirred in the dark for 30 min to eliminate the adsorption/desorption equilibrium effects before the irradiation. Part of the solution (5 mL) was taken out and centrifuged to remove the catalysts for 10 min. The residual concentration of dyes was detected by Lambda 25 UV–vis spectrophotometer (Perkin-Elmer, USA). The maximum absorption peak of MO, QB, RhB and were at 463 nm, 638 nm, and 553 nm respectively.

3. Results and discussion

The preparation process is very simple and the reaction conditions are quite mild. $Bi(NO_3)_3{\cdot}5H_2O$ and the ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) (as a Cl source) were first dispersed in solvents, such as water, ethanol and *N*,*N*-dimethyl formamide (DMF), then the mixture was kept stirring for 20 min at room temperature and followed by ultrasonic irradiation for 10 min, and the precipitate was obtained by filtered and washed with water and ethanol several times.

3.1. XRD analysis

First, the effect of solvents on the phase structures of the obtained BiOCl was investigated via XRD measurement. The XRD patterns of BiOCl prepared via ionic liquid assisted ultrasonic method at room temperature in water, ethanol and DMF are shown in Fig. 1a, where it can be seen that all the peaks are readily indexed to the BiOCl (JCPDS card no. 06-0249). No characteristic peaks of other impurities and undecomposed reactants are observed, demonstrating the high purity of the as-prepared samples. And the narrow sharp peaks indicate that the as-prepared BiOCl products are well crystallised. To be mentioned, the reaction solvent has a significant effect on the intensity ratio of the diffraction peak of {110}–{102}, which are 0.99, 0.43, and 0.35 for the BiOCl (DMF), BiOCl (H_2O) and BiOCl (C_2H_5OH) prepared in DMF, water and ethanol, respectively. And this gives the photocatalyst with different photocatalytic activity [14].