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Preparation and formation mechanism of $BiOCl_{0.75}I_{0.25}$ nanospheres by precipitation method in alcohol–water mixed solvents

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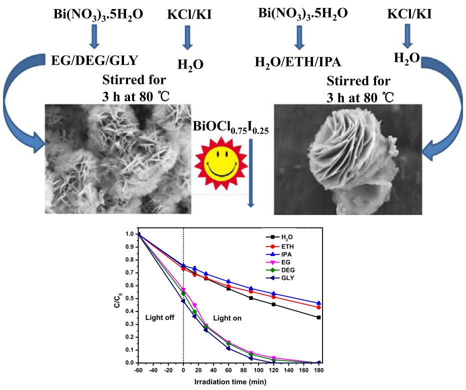
GRAPHICAL ABSTRACT



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ABSTRACT

$BiOCl_{0.75}I_{0.25}$ crystals with irregular three-dimensional (3D) flower-like and hierarchical nanosphere-like structures were successfully synthesized in different alcohol–water mixed solvents by precipitation method. The primary formation mechanism of $BiOCl_{0.75}I_{0.25}$ nanospheres was investigated by taking water, monohydric alcohols (ethanol and isopropanol), and polyhydric alcohols (ethylene glycol, diethylene glycol, and glycerol) as solvents in the synthesis process. The obtained $BiOCl_{0.75}I_{0.25}$ samples were characterized by powder X-ray diffraction, Raman spectroscopy, field emission scanning electron microscopy, and nitrogen adsorption. Results showed that the alcohol solvents with different physical and chemical properties used in the synthesis process performed significant functions in directing the morphology and surface pore structure of $BiOCl_{0.75}I_{0.25}$ crystals. Meanwhile, $BiOCl_{0.75}I_{0.25}$ synthesized in various solvents exhibited morphology-dependent adsorption and photocatalytic degradation abilities in removing *p*-hydroxyphenylacetic acid (*p*-HPA), which was used as a model pollutant, in aqueous solutions under simulated solar light ($\lambda \geqslant 290$ nm). In addition, the fabrication process of the crystal products was proposed through a series of time-dependent experiments.

1. Introduction

In recent years, heterogeneous photocatalysis that employ semiconductor materials has garnered considerable interest

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because of its excellent applications in environmental wastewater treatment [1,2]. As one of the most promising photocatalysts, TiO_2 has been extensively studied in the photocatalytic degradation of toxic organic compounds under ultraviolet (UV) light [3,4]. However, UV light accounts for less than 4% of the solar energy that reaches the earth surface, thereby limiting the effective use of sunlight [5,6]. The exploration of visible light-driven catalysts has long been a topic of research interest for establishing energy-saving wastewater treatment technologies. Bismuth and related compounds have become hot research topics because of their unique optical properties and photocatalytic activities [5,6]. In particular, BiOX (X = Cl, Br, and I) constitute a type of newly exploited efficient photocatalysts, whose light response can be tuned from UV light to visible light range because of different band gaps [7,8]. BiOX possesses a tetragonal layered structure, with $[Bi_2O_2]$ slabs interleaved by double slabs of halogen atoms, which is excellent for the efficient separation of electron–hole pairs [9].

With the intensive development of materials research, numerous kinds of BiOX crystals have been synthesized by solvothermal/hydrothermal [10–16], hydrolysis [17–20], precipitation [21], and sol–gel [22] methods. Catalysts with various configuration and morphologies have been obtained through different synthesis methods. In previous researches, one-dimensional (1D) nanostructured BiOX materials, such as fibers [23] and nanowire arrays [24], have been investigated in detail. Moreover, two-dimensional (2D) BiOX crystals displaying nanoplate-like [25], nanosheet-like [26], square-like [27], and lamellar structures [28,29] have been synthesized successfully, all showing promising photocatalytic activities. However, three-dimensional (3D) BiOX crystals possessing flower-like [10,11,13,15,17,30] or microsphere-like [12,14,16,20] morphologies have received the most interest due to specific properties. In fact, in comparison with 1D and 2D nanostructures, 3D hierarchical nanostructures are more efficient for solar energy storage and conversion. These structures can improve light harvesting and result in faster interfacial charge separations by supplying more reactive sites, thus enhancing photocatalytic efficiencies [31]. Various efforts have been focused on optimizing the surface feature of 3D structured BiOX materials to fully develop their unique properties. Except for the addition of special capping agents, such as the surfactants polyvinylpyrrolidone (PVP) [14,18,20], polyacrylamide (PAM) [11], or cetyltrimethylammonium bromide (CTAB) [15,16], to the synthesis reaction process, solvents change in the reaction media also covered a large proportion of studies.

In a previous paper, Xiao et al. transferred random BiOI platelets to hierarchical microspheres by replacing only water with ethanol (ETH) in the reaction media via precipitation [32]. Wang et al. successfully synthesized microflower-constructed BiOCl in a glycerol (GLY)–H_2O mixed solvents and nanoplate-constructed BiOCl in sole water by solvothermal method [13]. Kim et al. also used the solvothermal method to form 3D flower-like and 2D plate-like microstructured $BiOCl_xI_{1-x}$ in ethylene glycol (EG) and water solvents respectively [33]. As mentioned above, all the 3D BiOX catalysts exhibited considerably superior photocatalytic abilities than the 2D materials. Solvents evidently performed important functions as structure-directing agents in the catalyst synthesis process because of their special physical and chemical properties. The majority of solvents involved in the reaction media included certain types of alcohols, especially polyols like EG [10,33–38], diethylene glycol (DEG) [35,39], and GLY [13,40]. To date, literatures on the alcohol-assisted formation mechanisms of the BiOX catalyst were almost exclusively aimed at solvothermal method, which was usually investigated by conducting time-dependent experiments or changing alcohols [35,36,40]. However, the mechanisms of alcohol-assisted synthesis via precipitation method still remain unclear. Meanwhile, precipitation method offers several advantages, such as relatively lower temperature, ambient pressure, and shorter reaction time in comparison with solvothermal method [19,20,30]. Therefore, investigating the formation mechanisms of BiOX materials via precipitation method is of considerable importance.

In our previous studies, a series of $BiOCl_xI_y$ catalysts were synthesized by precipitation method in an EG–H_2O mixed solvents [41]. $BiOCl_{0.75}I_{0.25}$ exhibited the best removal activities in degrading *p*-hydroxyphenylacetic acid (*p*-HPA) in aqueous solutions under solar irradiation [21,41]. The main objective of the present paper is to better understand the mechanisms of crystal fabrication processes in the alcohol–water mixed solvents via precipitation method. Therefore H_2O, ETH, isopropanol (IPA), EG, DEG, and GLY were adopted as solvents to synthesize $BiOCl_{0.75}I_{0.25}$ catalysts. At the same time, time-dependent experiments were conducted to help verify the processes. The as-prepared $BiOCl_{0.75}I_{0.25}$ samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM), and N_2 sorption. The photocatalytic abilities of the $BiOCl_{0.75}I_{0.25}$ catalyst were also evaluated through the removal of *p*-HPA under simulated solar light, and the formation mechanisms of $BiOCl_{0.75}I_{0.25}$ catalysts by precipitation method were proposed.

2. Experimental

2.1. Materials and synthesis of $BiOCl_{0.75}I_{0.25}$ composites

$Bi(NO_3)_3 \cdot 5H_2O$, KCl, KI, ETH, IPA, EG, DEG and GLY were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). *p*-HPA was purchased from Aladdin Reagent Co., Ltd. All the reagents were analytical grade and used without further purification. Deionized water was used throughout the experiments.

The detection and quantification of *p*-HPA by HPLC was presented in our last paper [41]. As in the synthesis method in our previous papers [21,41], 12 mM $Bi(NO_3)_3 \cdot 5H_2O$ was added into 24 mL water or other five different alcohols (Table 1). The solution was stirred continuously at 80 °C for 20 min. KCl and KI at a molar ratio of 0.75:0.25 were dissolved in 96 mL deionized water, maintaining equal total molar amount to that of the molar amount of $Bi(NO_3)_3 \cdot 5H_2O$. The aqueous solution was added dropwise into the previous alcohol solution, and the pH of the mixture was adjusted to 9.0 with NH_3. In the entire process, the solution was stirred continuously and kept for 3 h at 80 °C. Finally, the mixture was separated by centrifugation at a speed of 12,000 rpm, washed for several times with deionized water and ethanol, and dried at 60 °C for 12 h. The as-prepared samples can be regarded as $BiOCl_{0.75}I_{0.25}$–H_2O, $BiOCl_{0.75}I_{0.25}$–ETH, $BiOCl_{0.75}I_{0.25}$–IPA, $BiOCl_{0.75}I_{0.25}$–EG, $BiOCl_{0.75}I_{0.25}$–DEG, and $BiOCl_{0.75}I_{0.25}$–GLY.

2.2. Characterization

The crystal phase structure was characterized by XRD (Bruker D8 Advance) using Cu Kα radiation (40 kV and 40 mA) as X-ray source (λ = 0.154056 nm) with a 2θ scope of 10–90°. The Raman spectroscopy for samples were attained by using a laser Raman spectrometer (Xplo, HORIBA JobinYvon, France) with laser excitation energy of 532 nm. The morphology and chemical compositions of the photocatalyst were observed through FESEM (Ultra 55, Germany, with an energy dispersive X-ray (EDX) microanalysis system). The surface area and pore distribution of the catalysts were determined by N_2 adsorption and desorption and using the multipoint Brunauer–Emmett–Teller (BET) analysis methods by an AUTOSORB-1 N_2 adsorption apparatus (Quantachrome, USA).