



A facile and rapid room-temperature route to hierarchical bismuth oxyhalide solid solutions with composition-dependent photocatalytic activity

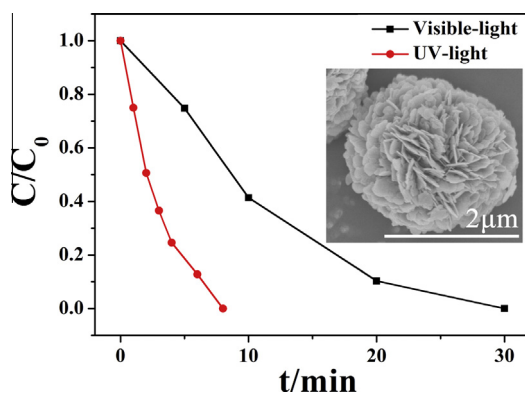


Juan Zhang, Qiaofeng Han*, Junwu Zhu, Xin Wang

Key Laboratory for Soft Chemistry and Functional Materials, Ministry of Education, Nanjing University of Science and Technology, Nanjing 210094, China

GRAPHICAL ABSTRACT

Flower-like $\text{BiOCl}_{0.5}\text{Br}_{0.5}$ solid solution obtained from Bi_2O_3 via a facile and rapid room temperature reaction exhibits excellent photocatalytic activity for RhB degradation under both UV and visible-light irradiation.



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ABSTRACT

The unique nanosheet-based flower-like $\text{BiOCl}_{1-x}\text{Br}_x$ ($x = 0-1$) hierarchical solid solutions have been prepared by the reaction of Bi_2O_3 and KCl/KBr in mixed solution of glacial acetic acid (HAc) and H_2O in dozens of minutes under ambient conditions. During the preparation process, the intermediate bismuth oxide acetate (CH_3COOBiO) plays a key role in the formation of $\text{BiOCl}_{1-x}\text{Br}_x$ solid solutions in such a short time. The as-prepared hierarchical $\text{BiOCl}_{1-x}\text{Br}_x$ solid solutions possess high specific surface areas and modified band structures, which exhibit enhanced photocatalytic activity for Rhodamine B (RhB) degradation in comparison with pure BiOCl and BiOBr under visible light irradiation, with the activity reaching the maximum at $x = 0.5$. The photodegradation efficiency of the $\text{BiOCl}_{0.5}\text{Br}_{0.5}$ solid solution is twice and 12 times higher than P25 TiO_2 under UV and visible light irradiation, respectively.

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1. Introduction

Eliminating various pollutants via semiconductor photocatalysis is one of the most promising solutions to environmental

* Corresponding author.

E-mail address: hanqiaofeng@njust.edu.cn (Q. Han).

pollution and energy crisis. TiO_2 is the most intensely studied due to its non-toxicity, chemical and thermal stability, low cost and high photodegradation activity toward almost all organic pollutants [1,2]. However, its band gap (3.2 eV) is too large for efficient utilization of visible light irradiation, as well as low quantum efficiencies, which restricts its practical application. Bismuth-based compounds, including Bi_2O_3 [3], BiOX ($X = \text{Cl}, \text{Br}$ and I) [4–6], $(\text{BiO})_2\text{CO}_3$ [7], Bi_2WO_6 [8], and so on, are gaining an increasing attention as potentially UV and visible light driven photocatalysts for pollutants degradation because of their suitable band positions, low toxicity and intrinsic polarizability induced by the $\text{Bi}^{3+} 6s^2$ lone pair of electrons which favors the separation of photogenerated electron-hole pairs. Among these bismuth-containing compounds, bismuth oxyhalides BiOX ($X = \text{Cl}, \text{Br}, \text{I}$) have demonstrated excellent photocatalytic activity due to their unique layered structure and layered-structure mediated internal electric fields between the $[\text{Bi}_2\text{O}_2]^{2+}$ positive slabs and halogen anionic slabs which could induce the separation of photogenerated electron-hole pairs and transfer from the bulk to the surface, and subsequent photocatalytic reactions on the surface [4]. In particular, a solid solution or composite containing more than one kind of halogen could be formed among different monomers, which possesses more effective photodegradation activity. For example, Huang group prepared $x\text{BiOBr}-(1-x)\text{BiOI}$ and $x\text{BiOI}-(1-x)\text{BiOCl}$ solid solutions respectively by adding CH_3COONa and $\text{NH}_3\cdot\text{H}_2\text{O}$ at room temperature with about 24 h of reaction, which displayed higher photocatalytic activity for methyl orange (MO) degradation than P25 under visible-light irradiation [9,10]. BiOI/BiOCl composite obtained after 20 h of reaction at room temperature exhibited higher activity for NO removal than single BiOI [11]. Lin et al. prepared double visible light excited BiOI/BiOBr composite by a facile room temperature anion-exchange strategy [12]. $\text{BiO}_x\text{Cl}_y/\text{BiO}_m\text{I}_n$, $\text{BiOCl}/\text{BiOBr}$, $\text{BiO}(\text{Cl}_{1-x}\text{Br}_x)$ and I-doped BiOClBr composites have been respectively synthesized via hydrothermal or solvothermal route which presented stronger photocatalytic activity than their monomers [13–17]. More recently, Sasson et al. reported the preparation of $\text{BiOCl}_x\text{Br}_{1-x}$ solid solution at room temperature from the reaction of $\text{Bi}(\text{NO}_3)_3$ and cetyltrimethylammonium halides (CTAC and CTAB) with exceptional visible light photocatalytic activity [18]. However, most of these synthetic processes required high temperature, pressure and long reaction time. Developing a simple, rapid and surfactant free room-temperature route to prepare bismuth oxyhalide solid solutions still remains challenging.

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$) is usually used as the source of bismuth cation in the preparation of bismuth oxyhalides due to its availability and cheapness. But it is easily hydrolyzed to form into bismuth subnitrate, which is hard to generate pure bismuth oxyhalides at room temperature under neutral conditions. Therefore, $\text{NH}_3\cdot\text{H}_2\text{O}$ was added to speed the reaction [10,11], where the reaction completion needed more than 10 h. Or alternately, the reaction was accomplished under a hydrothermal or solvothermal condition [13–17]. Sasson group prepared flake-like $\text{BiO}(\text{Cl}_x\text{Br}_{1-x})$ by using glacial acetic acid (HAc) as cosolvent to dissolve $\text{Bi}(\text{NO}_3)_3$ and halide anions, where CTAC and CTAB simultaneously serve as Br^- and Cl^- suppliers and structure-directing agents [18]. However, the usage of organic precursors or surfactants is not environmentally friendly. In this work, unique flower-like $\text{BiOCl}_{1-x}\text{Br}_x$ ($x = 0-1$) hierarchitectures have been prepared by using HAc as both solvent and one of the reactants. It reacted with bismuth oxide (Bi_2O_3) to form water-soluble bismuth oxide acetate, which could easily react with aqueous KCl and KBr to generate the expected products. All the reactions were conducted at room temperature under ambient conditions and completed in dozens of minutes. The as-prepared $\text{BiOCl}_{1-x}\text{Br}_x$ solid solutions at $x = 0.5$ exhibited the highest photocatalytic activity for

Rhodamine B (RhB) decomposition under visible light irradiation with 100% degradation efficiency within 30 min.

2. Experimental

2.1. Chemicals

All of the other chemicals were purchased from Sinopharm Chemical Reagent Ltd. Co. (Shanghai, China) and were used as received without further purification. Commercial P25 TiO_2 was purchased from Degussa (Germany) as a reference catalyst. Bi_2O_3 was synthesized according to our previous work [19].

2.2. Synthesis of $\text{BiOCl}_{1-x}\text{Br}_x$ solid solutions

The $\text{BiOCl}_{1-x}\text{Br}_x$ ($x = 0, 0.25, 0.5, 0.75, 1$) solid solutions were prepared at room temperature under ambient conditions. In a typical procedure, Bi_2O_3 (0.47 g; 1 mmol) was added into 10 ml of HAc solution with continuous stirring for 20 min until the suspension changed from yellow to white. Then 30 ml of H_2O was added into it and a transparent solution was obtained. Finally, KCl and KBr powders with certain molar ratio were added into above solution and the mixture was stirred for 30 min. The white solid was collected by filtration, washed several times with deionized water and ethanol, and dried at 60 °C for 10 h.

For comparison, $\text{BiOCl}_{1-x}\text{Br}_x$ microspheres with different morphologies and size were prepared by using 40 mL of HNO_3 solution (3 M) instead of HAc solution to dissolve Bi_2O_3 or $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ instead of Bi_2O_3 to react with HAc solution under otherwise identical experimental conditions.

2.3. Characterization

X-ray diffraction patterns (XRD) were obtained on a Bruker D8 Advance X-ray diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.542 \text{ \AA}$) at a scan rate of $0.05^\circ 2\theta \text{ s}^{-1}$. Raman spectra were measured in a Renishaw Invia spectrometer. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on a Tecnai T20 microscope equipped with an energy dispersive X-ray (EDS) spectroscopy. Field-emission scanning electron microscopy (FESEM) was performed on a Hitachi S-4800 microscope. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI Quantera II SXM X-ray photoelectron spectrometer with monochromatized Al $K\alpha$ as the exciting source. The results obtained in the XPS analysis were corrected by referencing the C_{1s} line to 284.8 eV. The deconvolution curves of O and Br peaks were obtained with Gaussian-Lorentzian fits. The Brunauer-Emmett-Teller (BET) surface areas were determined by nitrogen sorption using a Micromeritics ASAP 2010 analyzer. UV-vis diffuse reflectance spectra (DRS) were obtained on a Shimadzu UV 2550 spectrophotometer, equipped with an integrating sphere, using BaSO_4 as a reference.

2.4. Photocatalytic experiment

The photocatalytic activity of the as-prepared samples was evaluated by using RhB as a model compound. The photocatalytic reactions were performed in a XPA-7 photochemical reactor (Nanjing Xujiang Machine-electronic Company, China). The distance between the solution and lamp was kept at 8 cm. Xe lamp (500 W/7 A, 420 nm cutoff filter) with the light intensity of 50 mW/cm^2 and mercury lamp (500 W/7 A) with the light intensity of 35 mW/cm^2 were separately used as visible light and UV light source. The integrated light intensity on the surface of the suspension was measured with a visible-light FZ-A radiometer

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