



Research Paper

Influence of the halide and exposed facets on the visible-light photoactivity of bismuth oxyhalides for selective aerobic oxidation of primary amines



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ABSTRACT

Bismuth oxyhalides BiOX (X=Cl, Br, I) are seldom applied as photocatalysts in organic synthesis. Herein, we investigated their potential for the aerobic oxidative coupling of benzylamine to *N*-benzylidenebenzylamine, as imines are important synthetic intermediates of pharmaceuticals and biologically active nitrogen-containing organic compounds. The influence of the halide and the exposed crystal facets on the photoactivity was investigated. BiOBr showed excellent photoactivity, surpassing BiOCl and BiOI, which have poor light absorption and oxidation ability, respectively. Three differently faceted BiOBr photocatalysts were synthesized. The {001}-faceted BiOBr exhibited higher intrinsic activity than the {010}- or {110}-samples due to efficient charge separation. However, surface area plays an important role as reactions usually occur at the catalyst surface. Because of their much larger surface area, the solvothermally-synthesized BiOBr microspheres with {110}-dominant exposed facet showed the highest photooxidative activity, with 100% conversion and 100% selectivity to *N*-benzylidenebenzylamine after 14 h visible light irradiation at room temperature using oxygen from atmospheric air. This work provides an economical, feasible, sustainable and green process for the synthesis of imines and illustrates the great potential of bismuth oxyhalides as photocatalysts for organic synthesis.

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1. Introduction

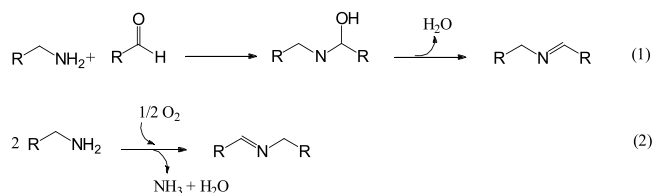
Imines are important synthetic intermediates of pharmaceuticals and biologically active nitrogen-containing organic compounds [1,2]. Traditionally, the synthesis of secondary imines involves condensation of primary amines with carbonyl compounds (mostly aldehydes) followed by dehydration (Scheme 1, reaction 1) [3,4]. However, aldehydes are extremely reactive and not easy to handle. Following environmental-benign concepts, the direct oxidation of primary amines to secondary imines using molecular oxygen (Scheme 1, reaction 2) will be a superior method. Ruthenium and gold-based catalysts, such as RuCl₃ [5], Ru-porphyrin [6], Ru/Al₂O₃ [7], Au/Al₂O₃ [8], Au/CeO₂ [9], and Au/graphite [10], have been found to be active for this reaction. Despite the use of precious metals, high temperature, typically > 100 °C, is required for the reaction. Very recently, photocata-

lysts such as TiO₂ [11], (Zn^{II}/Ti^{IV}) layered double hydroxide [12], and Nb₂O₅ [13], have been reported to catalyse the conversion of amines into imines at low temperatures with the assistance of UV light.

Visible light is more readily available than the higher energy UV radiation and research increasingly focuses on visible-light active photocatalysts. Mesoporous-C₃N₄ [14], CdS [15], Au-Pd/ZrO₂ [16], conjugated microporous poly(benzooxadiazole) networks [17], and hollow microporous organic networks [18] have been reported as active and highly selective catalysts for this reaction (≥99%). However, pure oxygen at high pressure is required, which translates into higher costs and increases the safety concerns for larger-scale production. To date, only Au/TiO₂ [19] and BiVO₄ together with a copper complex [20] can achieve 99% selectivity using atmospheric air as the oxygen source for benzylamine oxidation into secondary imines under visible light. However, for the former, a precious metal is necessary, which will add to the material cost while metal leaching during the reaction makes it difficult to reuse the catalyst. In the other example, an expensive and non-reusable copper complex has to be added together with BiVO₄ which poses problems in the product isolation. There-

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Scheme 1. Two ways for the formation of secondary imines.

fore, developing environmentally benign materials that work under mild conditions (atmospheric air and low temperature) with high selectivity remains a big challenge in this area.

Although bismuth is a heavy metal, it is considered as an environmental friendly element and its compounds are widely used in pharmaceuticals and cosmetics [21,22]. Bismuth compounds, such as BiOX [23–28], BiVO₄ [29,30], Bi₂WO₆ [31,32] and Bi₂O₃ [33,34] have been intensively studied as photocatalysts for pollutant remediation and hydrogen production. Especially the bismuth oxyhalides BiOX (X = F, Cl, Br, I) which crystallize in a tetragonal structure with alternating layers of [Bi₂O₂]²⁺ and negatively charged halogen ions have drawn much attention in water remediation and water splitting. However, research into their applications in organic synthesis is sparse. To the best of our knowledge, there is no report about bismuth oxyhalide for the photocatalytic oxidative coupling of primary amines to the corresponding imines.

In the present work, we synthesized BiOX (X = Cl, Br, and I) microspheres composed of nanosheets with different halides as well as BiOBr nanosheets with different exposed facets, i.e. (110), (001) and (010), and investigated their application as visible-light photocatalysts in the selective oxidation of benzylamine to *N*-benzylidenebenzylamine. It was found that both the halide and the exposed facets critically influence the catalytic activity. BiOBr microspheres, composed of nanosheets with (110) dominated facet, can catalyse the selective oxidation of benzylamine to *N*-benzylidenebenzylamine to realize a 100% conversion and 100% selectivity after 14 h visible light irradiation using atmospheric air at room temperature. The present work offers an easy-handling, economical, sustainable, and green process for the synthesis of imines and sheds light on the great potential of bismuth oxyhalides as photocatalysts for organic synthesis.

2. Experimental

2.1. Synthesis of BiOX

BiOX (X = Cl, Br, I) were synthesized by a solvothermal method. In a typical synthesis, solution A was prepared by dissolving 2 mmol of Bi(NO₃)₃·5H₂O in 10 ml of dimethylformamide (DMF) and methanol (5:5), while solution B contained 2 mmol of NaCl (or KBr, KI) in 0.1 ml H₂O, 5 ml DMF and 5 ml methanol. Solution B was added into solution A and after stirring for 30 min, the mixture was poured into a 40 ml Teflon-lined stainless steel autoclave and kept at 130 °C for 2 h under autogenous pressure. The resulting precipitate was collected by centrifugation, washed with absolute ethanol, and dried overnight in an oven at 80 °C. These samples are labelled as BiOX-S.

BiOBr exposing predominantly (001) facets (BiOBr-001) or (010) facets (BiOBr-010) were synthesized by pH variation following earlier literature [26]. Under acidic synthesis conditions, adsorption of H⁺ ions at the O-terminated (001) surface hinders growth in the [001] direction and therefore leads to the preferential formation of (001) faceted planes. At a higher pH of 6, the growth of other planes is favoured. For {010}-faceted BiOBr (denoted as BiOBr-010), 2 mmol Bi(NO₃)₃·5H₂O and 6 mmol of KBr were dissolved in 30 ml of deionized water and the pH was adjusted to 6 by addition

of 2 M NaOH. After stirring for 15 min, the solution was poured into a 40 ml Teflon-lined stainless steel autoclave and kept at 160 °C for 2 h under autogenous pressure. The resulting precipitate was collected by centrifugation, washed with absolute ethanol, and dried in an oven at 80 °C overnight. The sample prepared without adding any NaOH had a pH of 2.3 and was denoted as BiOBr-001.

2.2. Characterization

Powder X-ray diffraction patterns were measured with a Siemens D5005 diffractometer using Cu K_α radiation. The 2θ angle from 5 to 80° was scanned at 0.02°/s with a dwell time of 1 s/step. Nitrogen adsorption and desorption isotherms were measured at 77 K with a porosimeter (TriStar 3000, Micromeritics). The Brunauer-Emmett-Teller equation was used to calculate the specific surface area. Scanning electron microscopy (SEM) was performed on a JEOL JSM-6701F SEM (field-emission) microscope with 5 kV electron beam energy. Transmission electron micrographs were obtained with a JEOL 3010 operated at 200 kV. UV–vis diffuse reflectance spectra were measured with a Shimadzu UV-2450 UV–vis spectrophotometer. The adsorption of benzylamine on the samples was measured by equilibrating 100 mg BiOBr in various concentrations of benzylamine in acetonitrile (0.0025–0.04 M). Adsorption was carried out in the dark for 24 h and the benzylamine remaining in solution was determined by UV spectroscopy.

2.3. Photocatalytic activity

The photocatalytic amine oxidation was performed in an open glass tube (Fig. S1b) to allow access to atmospheric air for the continuous supply of oxygen. About 100 mg photocatalyst was suspended in 5 ml acetonitrile containing 0.1 mmol benzylamine. The sample was placed in a water bath at room temperature and irradiated with a 15 W Philips fluorescent lamp (λ ~ 400–650 nm) placed at a distance of 2.5 cm from the side of the tube. At regular time intervals, about 0.2 ml aliquots were removed and filtered through a syringe filter. The filtrates were analyzed by a gas chromatograph (HP 6890N) equipped with a HP-5 column and a FID detector. The identity of the peaks was confirmed by gas chromatography mass spectrometry (Shimadzu GCMS-QP5000). The conversion and selectivity were calculated based on the peak areas of the starting materials and all products including by-products.

A blank experiment was conducted under the same condition with only 5 ml acetonitrile in the glass tube to estimate the amount of solvent evaporation. Less than 3% of the solvent evaporated over the course of a 14 h experiment (Fig. S1), assuring that solvent evaporation did not significantly influence the results.

3. Results and discussion

3.1. Characterization

The BiOX samples were crystalline and their diffraction patterns fitted well with the corresponding tetragonal BiOX structures (BiOCl JCPDS No. 06-0249, BiOBr JCPDS No.09-0393, BiOI JCPDS No. 10-0045), respectively (Figs. 1 and S2). No extra peaks were found, showing the high purity of the samples. From scanning electron microscopy, the BiOX-S samples prepared by the solvothermal method are composed of nanosheets with thickness of ~ 30 nm aggregated into microspheres of 2–7 μm size (Fig. 2a–c). In contrast, BiOBr-001 and BiOBr-010 which were prepared without using organic solvents formed platelets but did not aggregate into microspheres (Fig. 2d & e). These platelets were bigger than those formed by the solvothermal synthesis. Their sizes are in the range of 0.5–3 μm with thickness of 100–200 nm for BiOBr-001 and 50–100 nm for BiOBr-010.

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