



Research paper

Chemical-bond conjugated BiO(OH)_xI_{1-x}-AgI heterojunction with high visible light activity and stability in degradation of pollutantsHuanhuan Ji^{a,b}, Lili Zhang^a, Chun Hu^{a,b,c,*}^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China^b University of Chinese Academy of Sciences, Beijing 100049, China^c School of Environmental Sciences and Engineering, Guangzhou University, Guangzhou 510006, China

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ABSTRACT

A layered BiO(OH)_xI_{1-x} solid solution was grown *in situ* on the surface of AgI particles by a one-pot co-crystallization method. Based on the results of XPS, EPR, XRD and other techniques, it was verified that a *p-n* heterojunction was formed through Ag-I-Bi cross-linking bonds in the interface of BiO(OH)_xI_{1-x} and AgI due to the common species of I⁻ ions. The resulting BiO(OH)_xI_{1-x}-AgI exhibited high efficiency and stability for photodegradation of phenolic compounds with visible light irradiation. No significant AgI decomposition or release of Ag⁺ or Bi³⁺ was observed in the photoreaction, and the photoactivity of AgI was enhanced almost 9-fold. These enhanced photocatalytic properties were attributed to the strong interfacial interaction between BiO(OH)_xI_{1-x} and AgI by the Ag-I-Bi bond junction. Due to the chemical-bond junction, the photogenerated electrons in the CB of AgI quickly transferred to the CB of BiO(OH)_xI_{1-x} to produce O₂^{•-}, while the holes in the VB of BiO(OH)_xI_{1-x} migrated to the VB of AgI to oxidize pollutants in water. The accelerated interfacial charge transfers were responsible for the high photostability and photoactivity of BiO(OH)_xI_{1-x}-AgI.

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1. Introduction

Photocatalysis is a promising technology to address the issues of the energy crisis and environmental pollution that have gained considerable interdisciplinary attention [1–3]. In order to utilize the inexhaustible and clean solar energy, appropriate semiconductors are required to carry out numerous catalytic reactions [4]. In recent years, a number of photocatalytic systems such as TiO₂, ZnO, CdS, g-C₃N₄ have been developed, and demonstrated that photocatalysis is a feasible technology.

Silver halides (AgX, X=Cl, Br, I), well-known photosensitive materials, have been intensively studied in the fields of photocatalytic hydrogen evolution and photodegradation of organic pollutants due to their prominent photoactivity. However, they are unavoidably decomposed into metallic Ag under visible-light irradiation. In illuminated AgX, the photo-generated electrons in the conduction band (CB) can be captured by surface lattice Ag⁺ ions

to form metallic Ag_n clusters, whereas the photo-generated holes oxidize lattice X⁻ to release X₂ [5]. Moreover, Ag⁰ would also be photo-corroded to Ag⁺ ions released to the water solution, causing secondary pollution during the reaction [6,7].

It has been proposed that the CB electrons of AgX can be quickly captured by another electron acceptor before reducing the lattice Ag⁺, which may not only improve the stability, but also enhance the photocatalytic efficiency. Several previous studies, such as those on Fe(III)/AgBr [5], GN-AgBr [8], and AgI/TiO₂ [9], have been devoted to accelerating the migration of photo-generated electrons from AgX.

Constructing a heterojunction is an effective strategy to enhance carrier transfer between semiconductors. When the heterojunctions are well-designed, the paths of carrier migration may even be regulated [10] to meet various needs in many works. More and more works have demonstrated semiconductor/AgX heterojunction structures exhibiting high photocatalytic efficiency, for example AgBr-BiOBr, Ag/AgBr/TiO₂ and Ag₃PO₄/AgI [11–13]. An efficient heterojunction requires matched band structures and tight contact between the two semiconducting materials, which can promote the smooth migration of electrons and holes in the interface [14,15].

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In recent years, materials possessing a laminated structure, such as graphene [16], $g\text{-C}_3\text{N}_4$ [17] and MoS_2 [18], have aroused much attention due to their excellent physico-chemical properties. Bismuth-based materials, composed of alternating layers of $[\text{Bi}_2\text{O}_2]^{2+}$ and inorganic groups, could efficiently separate photo-generated electron-hole pairs by internal static electric fields [19]. Using various inorganic anion ions, such as Br^- , I^- , CO_3^{2-} , OH^- etc. [20–22], it is easy to generate solid solutions of these $[\text{Bi}_2\text{O}_2]^{2+}$ -based laminar materials. Several Bi-based solid solution photocatalysts were reported to exhibit excellent and composition-dependent performance, such as $\text{BiOCl}_{1-x}\text{Br}_x$ [23], $\text{BiOBr}_{1-x}\text{I}_x$ [24], $\text{BiO}(\text{ClBr})_{(1-x)/2}\text{I}_x$ [25], BiO_xCl_y and BiO_xBr_y [26]. Thus, these materials are candidates for the construction of heterojunctions that could meet various requirements under different conditions.

In this work, the $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ solid solution was grown *in situ* on AgI particles by a one-pot co-crystallization method to produce a chemical-bond junction between the two phases. The AgI remained undecomposed throughout the whole photocatalysis reaction, and its photocatalytic activity for the degradation and mineralization of the tested phenolic compounds was greatly enhanced under visible irradiation, as it was combined with the $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ solid solution by chemical bonds. A preliminary effort to identify the correlation between the structural characteristics and photocatalytic performance has been undertaken.

2. Experimental

2.1. Chemicals and materials

The reagent 5-tert-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO) used as the spin trapping agent in the electron paramagnetic resonance (EPR) studies was purchased from the Bioanalytical Lab (Sarasota, FL). 2-chlorophenol (2-CP), 2, 4-dichlorophenol (2, 4-DCP), trichlorophenol (TCP), phenol, AgNO_3 , $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, *p*-Benzoquinone (*p*-BQ), Triethanolamine (TEOA) and all other chemicals were of analytical grade and purchased from the Beijing Chemical Company, and used without further purification.

2.2. Preparation of catalysts

The $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ -AgI composites were synthesized through a chemical co-precipitation method. In a typical process, 0.21 g of AgNO_3 in 2.3 mL of NH_4OH (25 wt% NH_3) was added to 200 mL ultrapure water. Then, 8.66 mL of a 0.2 M KI solution was added dropwise to the above solution, and subsequently, 0.24 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 10 mL of a 60 vol% acetic solution was added dropwise to the suspension and stirred at room temperature for 12 h. The generated precipitate was collected and washed several times with water to neutral conditions, and finally dried at 70 °C in air. $\text{BiO}(\text{OH})_x\text{I}_{1-x}$, and AgI samples were also synthesized under identical conditions but with AgNO_3 or $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ absent in the synthesis process, respectively. The *x* value in $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ -AgI and $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ samples were equal about 0.65 determined by the atomic ratio data from energy spectrum (EDS) results. And the content of $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ in the composite $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ -AgI were measured as 33.8 wt% using ICP-MS (inductively coupled plasma mass spectrometer) method when dissolved in H_2SO_4 solution.

As a reference, $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ was loaded on AgI ($\text{BiO}(\text{OH})_x\text{I}_{1-x}/\text{AgI}$) by a two-step method: 0.29 g of the as-prepared AgI was suspended in 200 mL ultrapure water, and 2.3 mL of NH_4OH and 2.46 mL of a 0.2 M KI solution was added subsequently. Then, 0.24 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 10 mL of a 60 vol% acetic solution was added dropwise to the suspension and stirred at room temperature for 12 h. The generated precipitate

was collected and washed several times with water to neutral conditions, and finally dried at 70 °C in air.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Scintag-XDS-2000 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$) operating at 40 kV and 40 mA. The morphological observations were performed by a field emission scanning electron microscope (SU 8020 FESEM; Hitachi). EDS results were obtained from a Hitachi S-3000N system. High-resolution transmission electron microscopy (HR-TEM) images were recorded using a JEOL-2010 TEM with an acceleration voltage of 200 kV. The electron paramagnetic resonance (EPR) of the solid powder samples and $\text{BMPO-O}_2^{\bullet-}$, $\text{BMPO}\cdot\text{OH}$ in solution were obtained using a Bruker model A300-10/12 electron paramagnetic resonance spectrometer. X-ray photoelectron spectroscopy (XPS) data were obtained using an AXIS-Ultra instrument from Kratos using monochromatic Al $\text{K}\alpha$ radiation and low-energy electron-flooding for charge compensation. All binding energies were calibrated by the C 1 s hydrocarbon peak at 284.80 eV. UV-vis diffuse reflectance spectroscopy (DRS, Hitachi UH4150) was also used to characterize the prepared samples. The photocurrent and Mott-Schottky analysis was performed using a basic electrochemical system (AMETEK Princeton Applied Research, Oak Ridge, TN) with a two-compartment, three-electrode electrochemical cell equipped with a photocatalyst photoanode (prepared by dip-coating and drying in air at 70 °C) and a platinum wire cathode in a 0.1 M Na_2SO_4 solution.

2.4. Photocatalytic degradation of pollutants under visible light irradiation

Photocatalytic experiments were performed in a beaker with aqueous suspensions of phenolic compounds (60 mL, 10 mg L^{-1}) containing 100 mg of catalyst powders, respectively. A 150-W Xe-arc lamp (Shanghai Photoelectron Device Ltd.) equipped with a wavelength cutoff filter to pass $\lambda > 400 \text{ nm}$ was used as the light source. The concentration of each chlorophenol was measured using high-performance liquid chromatography (1200 series; Agilent) with an Eclipse XDB-C18 column (5 μm , 4.6 \times 150 mm; Agilent). The released Ag^+ concentration during photoreaction was determined by an inductively coupled plasma mass spectrometer (ICP-MS, VG Plasma Quad 3). The total organic carbon (TOC) of each solution was measured with a TOC analyzer (TOC-VCPH, Shimadzu). The by-products of 2-CP photodegradation were detected using a Dionex ICS-2000 ion chromatography system with AS-DV auto-sampler. In trapping experiments, 3 vol% triethanolamine (TEOA), 1 mM *p*-benzoquinone (*p*-BQ), 5 mM $\text{K}_2\text{S}_2\text{O}_8$, 1 mM Na₃ and 100 mM *t*-butanol were added to the reaction suspensions as active species scavengers, respectively. In the recycling experiment, the photocatalyst was filtered and washed (the unwashed catalyst was also used after a statement) with ultrapure water prior to being resuspended in the 2-CP solution for another cycle.

3. Result and discussion

3.1. Characterization of photocatalysts

Fig. 1 shows the XRD patterns of $\text{BiO}(\text{OH})_x\text{I}_{1-x}$, $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ -AgI and AgI. The XRD pattern of $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ (Fig. 1a) is coincident with that of BiO_mI_n reported in the literature [27]. According to the synthetic process and literature reports [26], BiO_mI_n was formed by ion exchange of OH^- with I^- in $[\text{Bi}_2\text{O}_2]^{2+}$ layers, which could be best described as $\text{BiO}(\text{OH})_x\text{I}_{1-x}$, indicating its structural relationship to other $[\text{Bi}_2\text{O}_2]$ -based layered compounds. $[\text{Bi}_2\text{O}_2]\text{-(OH)}_2\cdot 2\text{H}_2\text{O}$ (BHO) [28] and BiOI were also prepared under otherwise identical

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