



Study on highly enhanced photocatalytic tetracycline degradation of type II AgI/CuBi₂O₄ and Z-scheme AgBr/CuBi₂O₄ heterojunction photocatalysts

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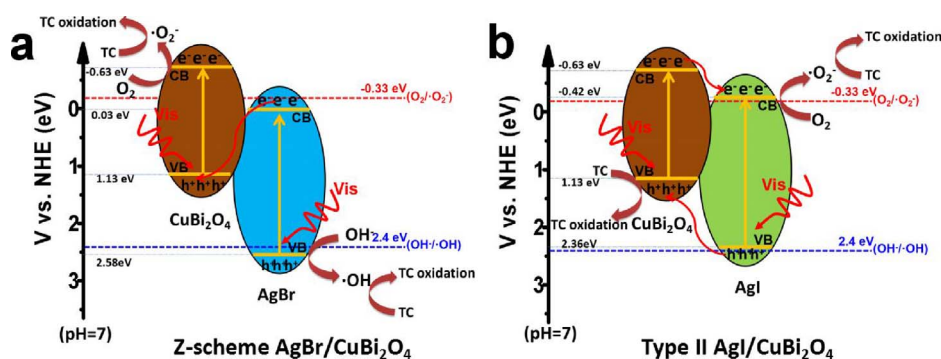
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GRAPHICAL ABSTRACT



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ABSTRACT

Removal of antibiotics from aqueous solutions by photocatalysis is an advanced technology for environmental remediation. Herein, we have fabricated a series of AgX (X = I, Br)/CuBi₂O₄ composites through an in-situ precipitation method. The photocatalytic activity of the obtained photocatalysts was measured by the degradation of tetracycline (TC) under visible light irradiation ($\lambda > 420$ nm). All the AgX (X = I, Br)/CuBi₂O₄ composites exhibit much higher photocatalytic activity than that of pure CuBi₂O₄. The enhanced photocatalytic activity is mainly attributed to the efficient interfacial charge separation and migration in the AgX (X = I, Br)/CuBi₂O₄ heterojunctions. Meanwhile, AgX (X = I, Br)/CuBi₂O₄ heterojunctions display excellent photocatalytic stability, and the photocatalytic degradation rates were not obviously decreased even after five successive cycles. Based on the energy band structure, the radicals trapping and electronic spin resonance (ESR) experiments, the Z-scheme mechanism of AgBr/CuBi₂O₄ and type II mechanism of AgI/CuBi₂O₄ heterojunction photocatalysts were tentatively discussed, respectively.

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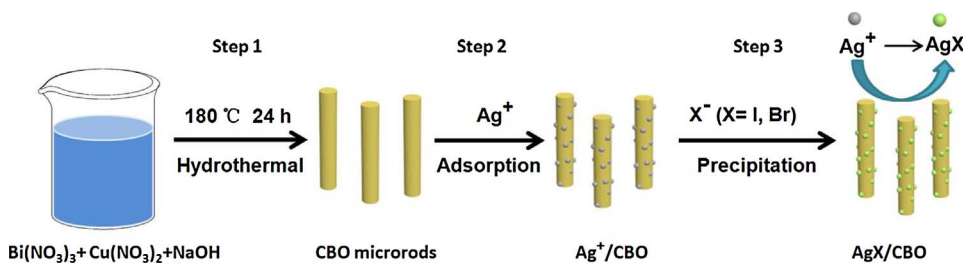


Fig. 1. Schematic illustration of the fabrication of AgX ($\text{X} = \text{I}, \text{Br}$)/CBO.

1. Introduction

Tetracycline (TC), as a broad-spectrum antibiotic, is widely accepted for treating a wide range of diseases, such as mycoplasmal pneumonia, hydatoncus, the diagnosis of malignant tumor epidemic typhus, etc. [1]. However, the continuous abuse and over-use of TC result in environmental pollution, which has drawn widespread concern in society [2]. Semiconductor photocatalysis has become one of the most advanced technologies for solving environmental problems owing to its low secondary pollution, economy and shorter periods [3]. During past decades, plenty of efforts have been mainly made to develop various semiconductor materials, including TiO_2 [4], ZnO [5], ZnS [6], CdS [7], CdSe [8] and so on. However, their practical applications have been limited by some negative factors, such as low photocatalytic activity under visible light, short-term stability against photo-corrosion and potential toxicity. Thereby, exploring low toxic and stable visible-light-driven (VLD) photocatalysts is still a hot spot in the field of photocatalysis.

CuBi_2O_4 (CBO), a promising semiconductor with narrow band gap of about 1.8 eV, possesses strong visible light response, excellent photostability and good photocatalytic activity [9]. However, the photocatalytic activity of solo CBO is still not satisfied due to its rapid recombination of electron-hole pairs. Various strategies have been explored to improve the photocatalytic performance of CBO, including regulation of different morphologies [10–12], doping with metal elements [13], coupling with carbon material [14] and building heterostructures [15]. Among of them, construction of CBO-based heterojunction photocatalysts, such as TiO_2/CBO [16], CuO/CBO [17], WO_3/CBO [18], BiVO_4/CBO [19] and so on, is demonstrated to be one of the most forward-looking ways owing to the efficient separation of electron-hole pairs.

Silver halides AgX ($\text{X} = \text{Br}, \text{I}$) are outstanding photosensitive materials and widely used in photo-graphic films, which indicates they possess potential ability in photocatalysis [20,21]. Nevertheless, large particle size and instability over pure AgX crystal forms lead to the decreased photocatalytic activity and low utilization rate in photocatalysis [22]. Fortunately, after coating AgX particles on certain semiconductor materials to form Z-scheme heterojunctions (eg. AgI/BiVO_4 [23], $\text{AgI}/\text{Bi}_5\text{O}_7\text{I}$ [24], $\text{Ag}/\text{AgBr}/\text{Bi}_{20}\text{TiO}_{32}$ [25], $\text{Ag}/\text{AgBr}/\text{g-C}_3\text{N}_4$ [26], etc) or traditional type II heterojunction photocatalysts (such as $\text{AgBr}/\text{Bi}_2\text{Sn}_2\text{O}_7$ [27], $\text{AgBr}/\text{Bi}_2\text{WO}_6$ [28], $\text{AgI}/\text{Bi}_2\text{MoO}_6$ [29], $\text{AgI}/\text{g-C}_3\text{N}_4$ [30], etc), the photocatalytic activity and stability of pure AgX particles have been improved. This inspired us to constitute the series of AgX ($\text{X} = \text{Br}, \text{I}$)/ CuBi_2O_4 (AgX/CBO) composites, in which CBO as a substrate to disperse AgX particles is not only conducive to avert AgX particles aggregation, but also to enhance the photocatalytic activity of CBO. To the best of our knowledge, there has no report about the synthesis of AgX/CBO heterojunction photocatalysts so far. Also, further effort should be required to investigate the charge transfer process and the mechanisms of AgX/CBO composites. In addition, considering that the content of AgX is very high in the pioneering AgX -containing heterojunction composites [22], which imperceptibly increased the cost of synthesized photocatalysts, we deliberated to decrease the AgX content (no more than 10 mol%) and designed cost-effective and high-efficient VLD photocatalysts for the degradation of TC.

In this work, AgX ($\text{X} = \text{Br}, \text{I}$)/CBO composite photocatalysts were successfully prepared via in-situ precipitation method. And the photocatalytic activity of AgX ($\text{X} = \text{Br}, \text{I}$)/CBO photocatalysts was measured though the degradation of TC under visible light irradiation ($\lambda > 420\text{ nm}$). The stability of $\text{AgBr}/\text{CuBi}_2\text{O}_4$ and $\text{AgI}/\text{CuBi}_2\text{O}_4$ photocatalysts was evaluated by five-run cycling tests. Based on the radicals trapping experiments, electron spin resonance (ESR) tests and experimental results, the mechanisms of AgX ($\text{X} = \text{Br}, \text{I}$)/CBO heterojunctions were discussed in detail.

2. Experimental section

2.1. Synthesis of CBO microrods and AgX/CBO composites

The general process for the fabrication of AgX ($\text{X}^- = \text{I}, \text{Br}$)/CBO is illustrated in Fig. 1. At first, the CBO microrods were prepared through a hydrothermal method. Typically, 2.42 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.6 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.87 g NaOH were mixed into 80 mL deionized water and stirred for 3 h. Then, the resulted slurry was transferred into a 100 mL Teflon-lined stainless steel autoclave, and then heated at $180\text{ }^\circ\text{C}$ for 24 h. The formed powders were washed with distilled water for three times and finally dried at $70\text{ }^\circ\text{C}$ in the oven. The synthesis process of AgX ($\text{X}^- = \text{I}, \text{Br}$)/CBO composites is as follows: 0.4 mmol of CBO powders were dissolved into 50 mL of water of containing different volumes of AgNO_3 solution (0.2 M) and intensively stirred for 3 h to stabilize Ag ion. Next, a certain amount of KX ($\text{X}^- = \text{I}, \text{Br}$) solution (0.2 M) were added and stirred for another 3 h in dark. Then the resulting precipitate was centrifuged, washed with deionized water and dried at $70\text{ }^\circ\text{C}$ in the oven. Thus, AgX ($\text{X}^- = \text{I}, \text{Br}$)/CBO hybrid photocatalysts with different molar ratios of AgX were prepared. The molar ratios of AgX ($\text{X}^- = \text{I}, \text{Br}$) in CBO composites are 0.5%, 1%, 3%, 5% and 10% and are denoted as 0.5% AgX/CBO , 1% AgX/CBO , 3% AgX/CBO , 5% AgX/CBO and 10% AgX/CBO , respectively. The pristine AgX ($\text{X}^- = \text{I}, \text{Br}$) powders were prepared under the same conditions in the absence of CBO powders.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded using an X'Pert-ProMPD (Holand) D/max- γ A X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154178\text{ nm}$). Scanning electron microscopy (SEM) images and energy dispersive X-ray analysis spectroscopy (EDX) were characterized by an FEI-Quanta 200 scanning electron microscope. Transmission electron microscope (TEM), high-resolution TEM (HRTEM) was performed with a FEI-Tecna F20 microscope operating at 200 kV, respectively. X-ray photoelectron spectroscopy (XPS) was performed on a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatized $\text{Al K}\alpha$ X-ray source. Room temperature UV–vis absorption spectra were recorded on a Lambda 750 (Perking Elmer) spectrophotometer in the wavelength range of 200–800 nm. Photoluminescence (PL) study was recorded on a Fluorolog-TCSPC Luminescence Spectrometer. Electrochemical analysis was conducted on a CHI 660b workstation. The Pt wire, a calomel electrode, and the samples were served as the counter electrode, the reference electrode, and the working electrode in a three-electrode cell.

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