



Enhanced visible-light-driven photocatalytic activity of $\text{Bi}_{12}\text{O}_{15}\text{Cl}_6/\text{Bi}_2\text{WO}_6$ Z-scheme heterojunction photocatalysts for tetracycline degradation

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ABSTRACT

Bismuth oxychloride ($\text{Bi}_{12}\text{O}_{15}\text{Cl}_6$), as a new bismuth compound photocatalyst, emerges excellent visible-light photocatalytic activity. Herein, a novel Z-scheme heterojunction photocatalyst of $\text{Bi}_{12}\text{O}_{15}\text{Cl}_6/\text{Bi}_2\text{WO}_6$ (BOC/BWO) was firstly synthesized via a facile solvothermal-calcining method. The crystal structure, morphology, energy band and photocatalytic performance of the as-prepared samples were investigated by multiple physicochemical techniques. The BOC/BWO sample with a molar ratio of 2:1 exhibited the highest TC degradation rate in comparison with that of all samples, which could reach 81.2% within 1 h under the visible-light irradiation. The reactive species trapping experiments and electron spin resonance results indicated that the superoxide radicals and photogenerated holes are the major active species in the photodegradation of TC. According to the photocurrent measurements, electrochemical impedance spectra and photoluminescence spectra, the greatly enhanced photocatalytic activity of BOC/BWO Z-scheme heterojunction could be attributed to high separation efficiency of photogenerated electron-hole pairs.

1. Introduction

With the characteristics of huge reserves and no secondary pollution, solar energy is considered to be one of the most important clean energy in 21st century [1,2]. In the premise of environmental pollution and energy shortages, semiconductor photocatalysts have a broad application prospect in organic pollutants degradation and water splitting due to their ability to convert solar energy into chemical energy directly [3–9]. Typical photocatalysts, such as TiO_2 and BiOCl , have been studied for many years in water purification, hydrogen evolution and selective oxofunctionalization [10–14]. However, these photocatalysts only respond to UV-light and a small part of visible-light due to the wide band gap and unsuitable band structure, which limits their further application. Therefore, it is necessary to explore more novel efficient visible-light-driven photocatalysts to meet the actual application requirements.

As a novel low toxicity photocatalyst, bismuth compounds have been extensively studied for decades due to their high photocatalytic activity in organic pollutants degradation, water splitting and CO_2 reduction, such as Bi_2WO_6 , BiVO_4 , $\text{Bi}_3\text{O}_4\text{Cl}$, $\text{Bi}_{12}\text{O}_{17}\text{Cl}_6$ and etc. [15–24]. Sillén-Aurivillius compounds has drawn increasing attention in recent years due to their unique $[\text{Bi}_2\text{O}_2]$ and $[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ alternating structure that be able to build internal electric field (IEF) [25,26],

which can accelerate the photogenerated charge separation and improve the photocatalytic activity [27–29]. Recently, $\text{Bi}_{12}\text{O}_{15}\text{Cl}_6$ (BOC), a typical Sillén-Aurivillius compound with narrow band energy, has been synthesized successfully via hydrothermal process, which exhibited superior photocatalytic activity for degrading of Bisphenol A (BPA) under visible-light irradiation [30]. However, the photocatalytic activity of BOC is still limited by low visible-light absorption efficiency and fast photogenerated charge carriers recombination rate. Hence, it is indispensable to enhance the photocatalytic activity of BOC by improving the visible-light absorption and the separation efficiency of photogenerated charge carriers.

To develop more photocatalysts with practical value, and further improve the solar-to-chemical conversion efficiency of their photocatalysis process, a series of methods were developed to extend the lifetimes of photogenerated electron-hole pairs and the visible-light absorption, including exfoliation, doping, engineering vacancies, constructing heterojunction, etc. [31–37]. Among them, construction of heterojunction is believed to be one of the important strategies to improve the photocatalytic activity, which can prevent the recombination of photogenerated carriers efficiently [38,39]. Recently, Z-scheme structure has been developed as a novel heterojunction system due to its obvious enhancement of photocatalytic activity compared with the general heterojunction [40–41]. Generally, the Z-scheme structure is

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composed of two different semiconductors with staggered band structures, which the conduction band (CB) of one component should be close to the valence band (VB) of another so that the electrons from the lower CB would recombine with the holes from the higher VB. Meanwhile, the remaining photogenerated electrons and holes can participate in reduction and oxidation reactions, respectively, wherefore the Z-scheme heterojunction system can perform a better reaction activity under visible-light illumination. However, there are only a few amount of photocatalysts are available for the practical application, further researches should be taken to explore more efficient Z-scheme structure systems.

Bismuth tungstate (Bi_2WO_6) is known as another important Sillén-Aurivillius compound as well as a visible-light-driven photocatalyst with a band gap of ~ 2.8 eV, which has been applied to photocatalytic organic pollutants degradation and O_2 evolution [42]. In previous studies, such as $\text{Bi}_2\text{WO}_6/\text{TiO}_2$, $\text{Bi}_2\text{WO}_6/\text{BiVO}_4$ and $\text{Bi}_2\text{WO}_6/\text{g-C}_3\text{N}_4$, have been reported that Bi_2WO_6 (BWO) and their heterojunctions play a key role in enhancing photocatalytic activity [43–45]. According to the band-structure and narrow gaps between BOC and BWO, it is feasible to construct a BOC/BWO heterojunction to improve the photocatalytic activity of BOC. To the best of our knowledge, there is no study about the BOC/BWO Z-scheme heterojunction and its photocatalytic performance research. In this study, BOC/BWO Z-scheme heterojunction was first fabricated by a simple solvothermal method and calcination. Series of BOC/BWO samples were synthesized by controlling the molar ratio of BOC and BWO. Compared with the pure BOC and BWO, the BOC/BWO Z-scheme heterojunction photocatalyst showed obvious enhancement of photocatalytic activity. To investigate the mechanism of the BOC/BWO Z-scheme heterojunction, electron spin resonance (ESR) analysis and active species detection experiments were conducted.

2. Experimental

2.1. Materials

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ($\geq 99.0\%$), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ($\geq 99.5\%$), NH_4Cl ($\geq 99.5\%$), ethylene glycol and glacial acetic acid ($\geq 99.5\%$) were purchased from Sinopharm Chemical Reagent. Tetracycline, triethanolamine, L-ascorbic acid and iso-propanol were used without further purification. The deionized water was used in all experiments.

2.2. Sample preparation

2.2.1. Synthesis of flower-like Bi_2WO_6 microspheres

Flower-like BWO was fabricated via a simple hydrothermal method [46]. In a typical synthesis, 0.5 mmol of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in a 40 mL mixture solvent (composed of 32 mL distilled water and 8 mL glacial acetic acid) to obtain a clear solution. Then, 1 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added to the above solution rapidly under vigorous stirring. After stirring for 1 h to ensure the reaction was uniform, the resulting reactant was transferred into a 50 mL Teflon-lined steel autoclave and maintained at 160°C for 12 h in an oven. Then, the reaction system was allowed to cool down to room temperature naturally. The resulting product was obtained by washing with distilled water and ethanol for three times to remove the residual ions, and drying at 60°C .

2.2.2. Synthesis of $\text{Bi}_{12}\text{O}_{15}\text{Cl}_6$ nanosheets

$\text{Bi}_{12}\text{O}_{15}\text{Cl}_6$ (BOC) was prepared via a facile solvothermal method and calcination [30]. In a typical synthesis, 2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.87 mmol of NH_4Cl were dissolved in 10 mL of ethylene glycol and 20 mL of distilled water, respectively. Then, the ethylene glycol solution was added into the aqueous solution drop by drop under vigorous stirring to obtain a white suspension. After stirring for 0.5 h, the suspension was transferred to a 50 mL Teflon-lined steel autoclave and heated at 160°C for 12 h in an oven and allowed to cool down to

ambient temperature. A white powder was obtained by washing with distilled water and ethanol for three times to remove the residual ions, and drying at 60°C . Then, the white powder was calcined in the Muffle furnace at a rate of 2°C min^{-1} and kept at 400°C for 5 h under air atmosphere to obtain a pale-yellow powder.

2.2.3. Synthesis of BOC/BWO Z-scheme heterojunction

BOC/BWO Z-scheme heterojunction was synthesized via a facile solvothermal method and calcination. In a typical synthesis, different amounts of BWO, which has been synthesized above, was added into 20 mL of deionized water with 0.87 mmol of NH_4Cl under vigorous stirring. Then, 10 mL of ethylene glycol solution with 2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added into the aqueous solution drop by drop under vigorous stirring to obtain a white suspension. After stirring for 0.5 h, the resulting reactant was transferred into a 50 mL Teflon-lined steel autoclave and heated at 160°C for 12 h in an oven. Then, the autoclave was allowed to cool down to ambient temperature and a white powder was obtained after centrifuging, washing and drying. Then, the white powder was calcined in the Muffle furnace at a rate of 2°C min^{-1} and kept at 400°C for 5 h under air atmosphere to obtain a pale-yellow powder. The BOC/BWO Z-scheme heterojunction with a molar ratio of 4:1, 2:1, 1:1, 1:2 and 1:4 are synthesized and named as WB-1, WB-2, WB-3, WB-4 and WB-5, respectively. For comparison, the mechanical mixing BOC/BWO sample with a molar ratio of 2:1 is synthesized and named as WB-M.

2.3. Characterization

X-ray diffraction (XRD) patterns of the as-prepared samples were characterized by a D/MAX-2500 diffract meter (Rigaku, Japan) with $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5405 \text{ \AA}$) at a scan rate of 7° min^{-1} to measure the crystal phase. Scanning electron microscopy (SEM) images were gathered on a Hitachi S-4800 field emission SEM (FESEM, Hitachi, Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analyses were obtained by using an F30 S-TWIN electron microscope (Tecnai G2, FEI Co.) with an accelerating voltage of 200 kV. Elemental mapping was used to determine the composition of BOC/BWO sample. To collect the UV-vis diffused reflectance spectra (DRS) of the samples, UV-vis spectrophotometer (UV2550, Shimadzu, Japan) was utilized with BaSO_4 as the reflectance standard. The electron spin resonance (ESR) analysis was conducted with an electron paramagnetic resonance spectrometer (A300-10/12, Bruker). For the photoluminescence (PL) spectra of samples, a fluorescence spectrophotometer (PerkinElmer LS 55) was used at room temperature.

2.4. Photocatalytic activity testing

The photochemical reactor was illuminated using a 250 W Xenon arc lamp with a UV-cutoff filter of 425 nm. At first, 50 mg of photocatalyst was added into 100 mL of TC aqueous solution with a concentration of 10 mg L^{-1} . Before visible-light irradiation, the mixed suspension was stirred in dark for 30 min to disperse evenly and ensure adsorption-desorption equilibrium. During irradiation, the cooling water was provided to keep the temperature of photochemical reactor at 25°C . During the photocatalytic process, about 3 mL of the suspension was taken out every 10 min. Before measurement, the suspension was centrifuged to obtain a clear solution by removing the photocatalysts, and the TC concentration was determined by a UV-vis spectroscopy (UV-1800, Shimadzu, Japan, $\lambda_{\text{max}} = 357 \text{ nm}$). The photocatalytic degradation ratio (DR) was calculated by the following formula:

$$\text{DR} = (1 - A_i/A_0) \times 100\% \quad (1)$$

A_0 is the initial absorbency of TC that reached absorption equilibrium, while A_i is the absorbency after the photocatalytic reaction.

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