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Flower-like Bi_2WO_6/ZnO composite with excellent photocatalytic capability under visible light irradiation

Juan Cheng [a], Yi Shen [a], Kuan Chen [a], Xi Wang [a], Yongfu Guo [a,b,*], Xiaoji Zhou [a], Renbi Bai [a,#]

[a] Center for Separation and Purification Materials &Technologies, Suzhou University of Science and Technology, Suzhou 215009, Jiangsu, China
[b] Jiangsu Collaborative Innovation Center of Water Treatment Technology and Material, Suzhou 215009, Jiangsu, China

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ABSTRACT

The photocatalytic ability of ZnO is improved through the addition of flower-like Bi_2WO_6 to prepare a Bi_2WO_6/ZnO composite with visible light activity. The composite is characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy with UV–vis diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy and N_2 adsorption-desorption isotherms. After modification, the band gap energy of Bi_2WO_6/ZnO is reduced from 3.2 eV for ZnO to 2.6 eV. Under visible light irradiation, the Bi_2WO_6/ZnO composite shows an excellent photocatalytic activity for degrading methylene blue (MB) and tetracycline. The photo-degradation efficiencies of (0.3:1) Bi_2WO_6/ZnO for MB and tetracycline are approximately 246 and 4500 times higher than those of bare ZnO, respectively, and correspondingly, the photo-degradation rates for the two pollutants are approximately 120 and 200 times higher than those with bare ZnO, respectively. Moreover, the photocatalyst of (0.3:1) Bi_2WO_6/ZnO exhibits a higher transient photocurrent density of approximately 4.5 μA compared with those of bare Bi_2WO_6 and ZnO nanoparticles. The successful recombination of Bi_2WO_6 and ZnO enhances the photocatalytic activity and reduces the band gap energy of ZnO, which can be attributed to the effective separation of electron–hole pairs. Active species trapping experiments display that $[O_2]^-$ is the major species involved during photocatalysis rather than •OH and h^+. This study provides insight into designing a meaningful visible-light-driven photocatalyst for environmental remediation.

1. Introduction

The colored organic dyes released from the textile and dye industries into water bodies are hardly biodegradable and can severely damage aquatic ecosystems and aquatic organisms. A recent report has shown that the global annual production of synthetic dyes and pigments has reached over 10^6 tons. In addition, 5%–15% of the synthetic dyes will usually be lost during the process of manufacturing and processing, and these waste dyes may be toxic or carcinogenic to aquatic organisms or systems in water [1]. Commonly, synthetic organic dyes used in textile industries (e.g., MB, $C_{16}H_{18}N_3SCl$, Reactive Orange-16 Dye and $C_{20}H_{17}N_3Na_2O_{11}S_3$) are considered as allergens, and some are mutagenic and carcinogenic. Moreover, the discharge of industrial wastewater containing synthetic dyes can cause serious contamination at the dumping site [2,3].

* Corresponding author. Tel: +86-512-68092987; E-mail: yongfuguo@163.com
# Corresponding author. E-mail: ceebairb@live.com
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So far, a variety of treatment methods, such as chemical precipitation/contaminant separation, coagulation, ozone oxidation, hypochlorite oxidation, electrochemical methods and adsorption, have been used to degrade organic dyes [4–9].

Recently, the use of antibiotics in medicine has considerably improved the treatment efficiency for infectious diseases and has also been widely used in agricultural production. However, with the increasing and extensive use of antibiotics, wastewater containing antibiotics are released into water bodies in large quantities, which has resulted in a serious environmental threat to aquatic and land ecological systems [10]. As one of the most typical antibiotics, tetracycline is widely used in medicine, agriculture and aquaculture. Unfortunately, tetracycline cannot be eliminated by natural environment or biological wastewater treatment technologies [11].

In previous studies, various strategies have been adopted to solve the problem of antibiotic wastewater. Biological removal processes, such as biodegradation by bacteria and fungi, and non-biological processes, including adsorption, hydrolysis, oxidation and reduction, have aroused widespread interest from the research community [12–17]. However, these methods have some inherent defects, including high cost, poor stability and low efficiency, which has limited the application of these technologies. Hence, the development of new technologies or materials to eliminate antibiotic pollution remains as a challenge in the field of environmental chemistry.

The photocatalytic degradation of organic pollutants under visible light or ultraviolet light is an important method, as it can quickly and thoroughly eliminate pollutants without leaving any harmful residue [18]. Semiconductors, which are extensively applied to electronic devices and integrated circuits, have recently been shown to be important photocatalysts in wastewater treatment technology and have been widely studied in the past few decades [19].

Wide band gap semiconductors, such as TiO_2 and ZnO, have been shown to be the most promising photocatalysts of all the semiconductor materials. It has been demonstrated that ZnO is a better photocatalyst than TiO_2, owing to its wide band gap (3.2 eV) and strong excitation binding energy (~ 60 meV). These characteristics have resulted in a lot of interest from many scholars for their use in electronics, light emitting diodes, gas sensing and photocatalysis [20].

However, ZnO has some inherent flaws, including a rapid recombination of photo-generated electrons and holes, low quantum efficiency, susceptibility to light corrosion, poor light stability, and so forth. These flaws greatly limit the photocatalytic potential and reduce the photocatalytic activity, which therefore limit the application of ZnO in environmental remediation.

Moreover, owing to its wide band gap, ZnO can only be excited by UV light, which only accounts for approximately 5% of the solar spectrum. This results in an ineffective absorption of visible light and low usage rate for sunlight [21]. Therefore, it is a challenging task to obtain a ZnO photocatalyst with both favorable light stability and high photocatalytic activity under visible light by doping or modifying methods, but this has now become a frontier subject in international research [22].

The modification of ZnO with other semiconductors, such as CdS [23], In_2S_3 [24], NiO [25], CdSe [26], PbS [27], Ag_2S [28], Mn_3O_4 [29], Bi_2O_3 [30], Cr_2O_3 [31], Bi_2S_3 [32] and Bi_2WO_6, is an effective method to generate a large number of electron–hole pairs and enhance the photocatalytic activity of ZnO. The research on Bi-based photocatalysts has long been a hot topic in the field of photocatalysis and many important candidates have been reported, including BiOCl [33], $Bi_{12}GeO_{20}$ [34], Bi_2SiO_5 [35] and BiOBr [36]. Among these semiconductors, as inorganic semiconductor nanocrystals, Bi_2WO_6 has received widespread consideration for its nontoxicity, suitable band gap and excellent photocatalytic performance [37–39].

As an efficient material to improve the catalytic properties of photocatalysts, heterojunction photocatalysts can be used to facilitate the separation of photo-excited electron–hole pairs. In general, when p-type and n-type semiconductors are in contact, they form a p-n junction with a space charge region between the interface of the two semiconductors owing to the diffusion of electrons and holes. Therefore, the construction of a semiconductor heterojunction has attracted a lot of attention owing to its effectiveness in improving the photocatalytic activity. Some new findings have been also reported on the semiconductor heterojunction photocatalysts, such as the p-n junctions of BiOI/$Bi_{12}O_{17}Cl_2$ [40], $BiVO_4$/BiOI [41] and BiOBr/BiOI [42]. These results provide an important theoretical foundation for this work.

In the present work, a heterojunction catalyst of Bi_2WO_6/ZnO was synthesized by a two-step hydrothermal method. The basic performance and photocatalytic properties were investigated through the degradation of MB and tetracycline. The aim was to improve the photocatalytic efficiency and enhance the conversion for solar energy through reducing the band gap energy of ZnO, increasing the effective separation of electron–hole pairs and promoting the transfer of charge carriers. Moreover, the degradation mechanism of a flower-like Bi_2WO_6/ZnO composite heterojunction photocatalyst was also proposed.

2. Experimental

2.1. Materials

Bismuth nitrate (99.0%), citric acid (99.5%), zinc acetate dihydrate, sodium tungstate, NaOH (96%), HNO_3 (65%–68%), $Na_2C_2O_4$, 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL), methylene blue (≥ 92%) and tetracycline (≥ 98%) were of analytical grade.

2.2. Preparation of photocatalysts

The Bi_2WO_6/ZnO heterojunction catalyst was prepared by the following two-step method [43]. The concentration and pH value of a NaOH solution can affect the morphology of as-prepared ZnO. When the concentration and pH of NaOH were 10 mol/L and 13, respectively, the morphology of the synthesized ZnO microspheres were flower-like. Therefore, the synthesis of flower-like ZnO was carried out as follows: zinc