Materials Letters 217 (2018) 296–299

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

One-step calcination preparation of worm-like ZnO@BiOI heterojunction with enhanced visible light response for mild photooxidation reaction

Zhifang Tong [a,1], Lingling He [a,1], Chunguang Ren [b], Zhonghua Wang [a,*], Zonglin Jiang [a,*]

[a] Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, College of Chemistry and Chemical Engineering, China West Normal University, Nanchong, Sichuan 637002, PR China

[b] Chinese Academy of Sciences, Shanghai Institute of Materia Medica, Yantai Branch, Yantai Institute of Materia Medica, Yantai, Shandong 264000, PR China

ARTICLE INFO

Article history:
Received 17 November 2017
Received in revised form 26 December 2017
Accepted 15 January 2018

Keywords:
One-step method
ZnO@BiOI
Nanocomposites
Visible light
Oxidation, 1,4-DHP derivatives

ABSTRACT

ZnO@BiOI nanocomposite has been prepared by a one-step calcination method and characterized by XRD, SEM and HRTEM. The photocatalytic activity of ZnO@BiOI nanocomposite was examined by the photooxidation of 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (1,4-DHP) under visible light irradiation ($\lambda > 400$ nm). Compared with pure ZnO and BiOI, the photocatalytic activity of ZnO@BiOI was dramatically enhanced. In addition, the 1,4-DHP was quantitatively converted to its pyridine derivatives by the mild oxidation without deep oxidation or degradation. Mechanism study showed that superoxide anionic radicals ($\cdot O_2^-$) and photogenerated holes (h^+) were the major active species.

1. Introduction

Semiconductor photocatalyst has attracted great interest due to the potential application in environmental remediation and energy transformation [1–6]. Among various semiconductors, ZnO has been extensively investigated owing to its high stability, low cost and nontoxicity [7–9]. However, ZnO is only responsive to UV light because of its wide band gap energy (~3.3 eV) [7,10]. Moreover, a high recombination rate of photoinduced electron-hole pairs also decreases the photocatalytic performance of ZnO semiconductor. These drawbacks largely limited the practical application of ZnO in the field of photocatalysis. One of the strategies to overcome these shortcomings is to combine ZnO with other narrow band gap semiconductors [11,12].

Bismuth oxyhalides (BiOX, X = Cl, Br, and I) are well known layered compounds that have a crystal structure of $[Bi_2O_2]$ layers interleaved by slabs of halide atoms [3]. Among BiOX compounds, BiOI, with a band gap of 1.8 eV, has the strongest absorption in visible light region, and is considered as an excellent visible light photocatalyst [3,13]. Recently, ZnO@BiOI composite materials have been fabricated by chemical bath method [3] and microwave-assisted solution method [14], and applied as heterojunction photocatalyst or adsorbent for the photodegradation or adsorptive removal of organic pollutants. However, to the best of our knowledge, ZnO@BiOI composite prepared by a one-step calcination method and utilized as a visible light photocatalyst for mild photooxidation reaction has not yet been reported. In this work, ZnO@BiOI composite was prepared by a one-step calcination method, and its photocatalytic activity was examined by the photocatalytic oxidation of 1,4-DHP under visible light irradiation. Results showed that the ZnO@BiOI composite exhibited remarkably enhanced visible light photocatalytic activity compared with pure ZnO and BiOI due to the formation of heterojunction structure. In addition, the 1,4-DHP was almost completely converted to its pyridine derivatives without deep oxidation.

2. Experimental

ZnO@BiOI was prepared by the calcination of zinc nitrate and bismuth iodide in a programmed muffle furnace. Briefly, 0.59 g of BiI_3 and 0.15 g of $Zn(NO_3)_2{\cdot}6H_2O$ were mixed in a mortar and ground to a homogeneous mixture. The mixture was transferred into a 30 mL crucible, calcined at 300 °C for 8 h with a heating rate of 3 °C min^{-1}, and then cooled to room temperature naturally.

Powder X-ray diffraction (XRD) datum was recorded on a Rigaku Dmax/Ultima IV X-ray diffractometer. Scanning electron microscopy (SEM) measurement was carried out on a Hitachi SU8010 scanning electron microscope. High-resolution transmission

* Corresponding authors.
E-mail addresses: zhwangs@163.com (Z. Wang), orgchem@cwnu.edu.cn (Z. Jiang).

[1] Both authors contributed equally to this work.

https://doi.org/10.1016/j.matlet.2018.01.083
0167-577X/

electron microscopy (HRTEM) was measured on an FEI Tecnai F20 microscope.

The photocatalytic activity of the ZnO@BiOI was evaluated by the photooxidation of 1,4-DHP under visible light irradiation. The visible light was provided by a 70 W metal halide lamp with a cut-off filter (λ>400 nm). Typically, 50 mg of ZnO@BiOI was dispersed into 50 mL of 0.1 mM 1,4-DHP H_2O/ethanol solution (v/v = 1:1). Prior to visible light irradiation, the mixture was magnetically stirred for 30 min to obtain an adsorption-desorption equilibrium. This reaction was monitored spectroscopically by measuring the absorption of 1,4-DHP at the wavelength of 374 nm [15].

3. Results and discussion

Two sets of XRD peaks could be identified in the XRD pattern of the ZnO@BiOI sample (Fig. 1A). The diffraction peaks denoted with * and # marks could be indexed to the tetragonal phase of BiOI (JCPDS No. 10-0445) and the hexagonal phase of ZnO (JCPDS No. 36-1451), respectively. SEM images showed that the ZnO@BiOI sample was composed of worm-like nanoparticles with diameter of about 50 nm (Fig. 1B and C).

Fig. 1D shows the HRTEM image of the ZnO@BiOI sample. The observed lattice spacings of 0.280 and 0.303 nm correspond to the (1 0 0) and (1 0 2) planes of hexagonal ZnO and tetragonal BiOI [16], respectively. The good crystallinity nature of ZnO@BiOI and clear interface between ZnO and BiOI revealed by the HRTEM are beneficial for the separation of electron-hole pairs [16].

The photocatalytic activity of the BiOI@ZnO was evaluated by the photooxidation of 1,4-DHP [15], which is the key component in a variety of bioactive compounds, such as anti-hypertensives [17], calcium-channel blockers [18], and cell proliferation modulators [19]. Fig. 2A shows the UV-visible spectral changes of 1,4-DHP under visible light irradiation (λ > 400 nm) in the presence of ZnO@BiOI. It can be seen that the absorption band at 374 nm gradually decreased with irradiation time, accompanied with the increase in intensity at ~280 nm, indicating the conversion of 1,4-DHP to its pyridine derivatives [15]. The absorbance at λ = 374 nm was only slightly decreased under visible light irradiation in the presence of pure ZnO or BiOI, suggesting a little bit conversion of 1,4-DHP (Fig. 2B and C). After 25 min of irradiation, the conversion percentages of 1,4-DHP were 97.1%, 3.8%, and 6.0% in the presence of ZnO@BiOI, ZnO and BiOI, respectively (Fig. 2D). The photooxidation of 1,4-DHP was negligible under only visible light irradiation without addition of any photocatalysts.

According to the UV–visible spectral evolution of 1,4-DHP [15], it is likely that 1,4-DHP is converted to its pyridine derivatives of 1b as shown in Fig. 3A. Mass spectroscopy (MS) was carried out to confirm this conversion. As shown in Fig. 3B, the measured molecular weight (MW) of 1,4-DHP was 253 Da, which was in agreement with the calculated MS (253.3 Da). After visible light irradiation for 10 min in the presence of ZnO@BiOI, two sets of MW peaks were observed, the MW of 253 Da was ascribed to 1,4-DHP, while the MW observed at 251 Da should be attributed to 1b, the dehydrogen product of 1,4-DHP (Fig. 3C). After 25 min of light irradiation, the MW peaks of 1,4-DHP almost disappeared, while the peaks for 1b was dominant in the MS spectrum (Fig. 3D). The MS spectral changes were well in agreement with the UV-visible spectral evolution. The absorption peaks at 374 and 280 nm correspond to 1,4-DHP (MW = 253 Da) and 1b (MW = 251 Da), respectively. The intensity decrease at 374 nm and increase at 280 nm are due to the conversion of 1,4-DHP to 1b.

The excellent photocatalytic performance of the ZnO@BiOI inspired us to examine the underlying photocatalytic mechanism. As shown in Fig. 4A, addition of isopropyl alcohol (IPA) as hydroxyl radicals (·OH) scavenger showed negligible effect on the

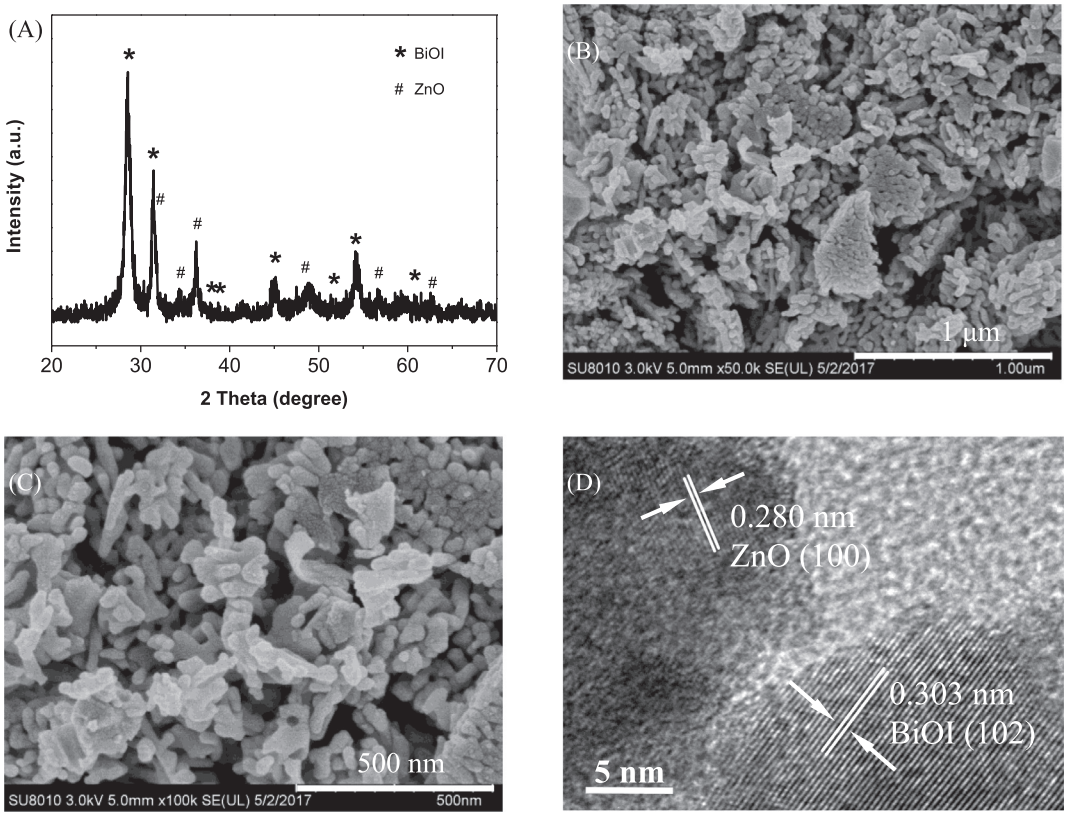

Fig. 1. XRD pattern, SEM and HRTEM images of BiOI@ZnO composite.